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THE PRINCIPLES AND PRACTICE

OF

TEXTILE PRINTING.

BY

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AND

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EDMUND KNECHT

8th December 1925

Doctor of Philosophy, Zürich University,
Master of Science, Manchester University,
Fellow of the Institute of Chemistry.

An esteemed Master, Friend and Collaborator.

Printed in Great Britain by
NEILL & Co., LTD., EDINBURGH.

PREFACE TO THE THIRD EDITION.

The favourable reception accorded to the second edition of this treatise on its appearance in 1924, and the generous support received subsequently, were particularly acceptable to the authors, inasmuch as it was thus indicated that the original work had fulfilled its purpose, that it had proved of practical use to those to whom it was addressed, and that, from the first, a steady interest had been maintained in its continuance as a handy book of reference to be modified and widened in scope as occasion dictated.

The second edition ran out of print three years ago, and enquiries for it have since been continuous. To reprint the work as it stood was neither possible nor desirable: the limited collection of printed textile patterns, which formed an integral part of it, had already been exhausted and could not be replaced at the time; and, more important still, it was evident that the work itself, viewed in the light of recent progress, had during its comparatively short life become in some degree out of date, requiring thorough revision and considerable extension if it were to be brought into closer consonance with present-day practice. Hence, a new issue being called for, it became necessary to submit the text of the last edition to a complete revision and collate and incorporate a large amount of fresh material in order to bring the subject-matter, as far as possible, up to date. To do this adequately has entailed re-setting most of the work—a necessity which has afforded an opportunity of recasting and emending the text more fully, and of making more copious and comprehensive additions to it, than any rearrangement of the old stereotype plates would have allowed.

For this opportunity the present writer is indebted to the Publishers, to whom he wishes here to express his keen appreciation of the confidence and enterprise with which they have, once again, embarked on the onerous and costly undertaking of producing a work on a subject of such narrow appeal.

During the twelve years that have elapsed since the last edition of this work was published, the trend of textile printing has been steadily towards increased fastness and brightness in colour and simplification of process; and, in both these directions, rapid and continuous progress has been made in all departments of the industry. Invention and improvement have gone on at a great pace and have influenced profoundly the general technical conduct of the industry.

The results of incessant scientific research, devoted by colour manufacturers and others to the elucidation of technical problems, have not only added enormously to the tinctorial resources of the textile printer, but have led to the introduction of many new and ingenious methods and styles, and also brought about numerous important changes in the manipulation of those of earlier date. Thus, all the older series of synthetic dyestuffs have been improved in quality and extended in range; many new colouring matters and dyestuffs of entirely new types and properties, and many auxiliaries, together with special processes for their application, have been introduced; much new and improved plant has been designed expressly to deal more speedily and efficiently with all classes of printed goods at every stage of their production; the printing of acetate rayon fabrics has been transformed from a specialised to a routine operation, and printing on other fabrics has been

developed in new directions; such old processes as have not been eliminated have been passed under review, and some of them modified with a view to obtaining a quicker output, a better yield, or a wider application; and many new processes, and combinations of processes, have been brought into use, which, in addition to being capable of ready adjustment to meet the requirements of changing demand, have provided means of producing a vast number of colour effects that, previously, were unobtainable, and have thus greatly extended the possibilities of the industry. For example, with the facilities now available, certain styles of work that, formerly, were restricted to one method of production and confined within very narrow chromatic limits, may to-day be produced not only in any desired combination of beautiful and permanent colours, but also by means of several alternative methods which yield results as good as, and often better than, those given by the original process.

Altogether, it may be taken that more practical advance, and advance over a wider field, has been made in the textile printing industry in the last ten or twelve years than during any similar period in the past.

It must not be supposed, however, that the swift current of invention has swept away the older methods of producing printed fabrics. Far otherwise: for just as our language has its foundations in the Latin tongue, so modern printing practice has its roots embedded in the processes of the past. In other words, the fundamental principles underlying the production of all printed textiles remain practically unaltered, though the actual processes whereby they are applied may have undergone considerable changes. It is true that many old processes and styles have become obsolete and have disappeared from modern practice, and that others, though still retained, are gradually being superseded; but a few standard styles, still produced by the old methods—*e.g.* the Madder dyed style, Turkey-red chintzes, oxidation discharges on dyed Indigo, Aniline black prints and resist styles, Indigo and Alizarin prints and cover and pad styles, the important Steam style, etc.—are yet in current use, and constitute no inconsiderable proportion of the total output of printed goods. The styles of the immediate past and those of the present differ principally in respect of quality of colour, those of the present being greatly superior in point of fastness, variety, and brilliancy; but all are still obtained by the old-established methods of direct printing, discharge and reserve printing, dyeing on printed mordants, printing one component of a colour on cloth prepared with another, or by stencilling: and, so far as technique is concerned, very little difference is to be discerned between the *types* of chemical reactions and mechanical operations involved in the production of such styles to-day and those employed for similar purposes in the past. What has happened, however, is that these typical reactions, operations and processes are now applied to an enormously extended range of materials and dyestuffs, and have become so modified, in adapting them to new conditions, that it is not always easy to trace their descent. In short, during the last ten or twelve years, many noteworthy changes and developments have taken place in the technique of textile printing and a formidable hiatus has been created between the practice of the beginning of this period and that of to-day. It is the aim of the present edition to fill in this gulf as far as it is possible to do so in dealing with an industry subject to rapid and continual progress.

The present issue, though described as a new edition, constitutes, in reality, an almost entirely new work, since not only has the text of its predecessor been thoroughly revised and expanded and, to a great extent, re-written, but a large number of new sections, dealing with the most recent advances

in the trade, has been inserted, and various appendices have been added by way of supplementing the information contained in the text proper.

The added matter, whilst it relates chiefly to the colour side of textile printing, includes descriptive notices of some of the latest improvements in: bleaching kiers, automatic mechanical pilers, steaming and ageing apparatus, mercerising plant, printing and padding machines, hot flues, and dyeing and washing becks; also a description of Screen printing, a form of stencilling that has lately come into prominence. Additional information is included relating to Basic, Mordant, Sulphur, and Direct colours generally, and to their uses in various discharge, reserve, and combined styles. In order to avoid overlapping, several new methods for the production of *fast* colour resist effects under Aniline black padded grounds have been excluded from the particular section devoted to Prud'homme styles and are described separately, in other parts of the work, as they arise in connection with the general application of recently introduced relevant colouring matters. Fast colour discharges on dyed Indigo have lost much of their importance since the introduction of Variamine blue, but as they are still in demand for certain markets, a description has been included of Haller's method of obtaining Vat (Indanthrene) colour discharges on Indigo grounds; also a process for producing similar effects on other Vat colour dyed grounds.

The remarkable progress in the development of the Vat and Azoic groups of dyestuffs which has been made during the past ten or fifteen years, has necessitated the rewriting of the whole of the matter relating to the properties and manifold applications of these two most important series of colouring matters. As regards the Azoic colours: Naphthol A.S. and its analogues, together with the numerous amino-bases and salts (Fast bases, Fast colour salts, etc.) associated with them in the production of Insoluble Azoic colours formed on the fibre, likewise their derivatives, the Rapid Fast, Rapidogen, and Rapidazol colours—consisting of mixtures of naphthols with various diazo compounds—are discussed at considerable length; and the chemical composition, and practical application to all styles of printing, of these different types of Azoic colours, are described in some detail. The Vat dyestuffs and their derivatives, the Indigosols and Soledons, are dealt with in like manner, full particulars being given of the many alternative methods in use for their application to all styles and fabrics. The new "Suprafix" brands of the Indanthrenes, and the Colloresine process of printing, are noted in the description of Vat colours.

The printing of wool and silk is much more fully dealt with in the present edition than in previous issues, the whole of the subject-matter having been re-written and greatly extended in order to take in the printing of wool and silk unions and various mixtures of wool and silk with cotton and rayon fibres.

An entirely new section has been added on the printing of the so-called artificial silks, viz. Viscose and Acetate rayons. In general, the technique of printing Viscose materials is the same as that for cotton goods, except that for certain dyed styles Viscose fabrics are unsuitable. On the other hand, Acetate rayon demands, for the most part, quite different treatment, and for this reason particular attention has been given to the difficulties encountered in printing it and to the special dyestuffs, processes, etc., which have been introduced for the purpose of overcoming these difficulties as far as may be.

Interspersed in the text additional information will be found on the following subjects, amongst others:—Thickening agents, including new preparations of starch and natural gums; synthetic mordants for Basic dyestuffs; Sericose; Opalogen for matt effects on rayon goods; and various auxiliary materials employed for softening, penetrating, wetting-out, dispersing and solvent purposes.

As before, a list is given of the more important intermediates and adjuncts used in printing and dyeing, together with their chemical composition (as far as is available) and the uses to which they are generally applied.

The 221 printed patterns contained in the text are all new and have been carefully selected to illustrate the processes and styles to which they refer: with very few exceptions, they have been produced under large-scale conditions and by the methods described. The bringing together, from many sources, of such a large collection of specially printed representative patterns, and its preparation for an edition of a book of this kind, are fraught with more difficulty and involve much more expense, assiduous work, and co-ordination than might be supposed by anyone unacquainted with such a task; but the author is of opinion that the examination of an actual pattern gives a far better idea of the possibilities of a colour or a process than can be visualised from a mere verbal description, and for this reason he believes that the provision of a range of typical examples of prints on various fabrics, produced according to the methods described, is well worth the trouble entailed.

The majority of the illustrations of machinery are also new and, for convenience of handling, have been reduced in size so as to fit into the text without folding.

There remains the pleasant duty of acknowledging help from many quarters in the preparation of this edition. To Messrs The Calico Printers' Association, Ltd., Messrs The Imperial Chemical Industries, Ltd. (Dyestuffs Group), Messrs F. Steiner & Co., Ltd., Messrs Horridge & Cornall, Ltd., Messrs The I.G. Farbenindustrie Aktiengesellschaft, Messrs The Society of Chemical Industry in Bâle, Messrs The Geigy Colour Co., Ltd., Messrs The Sandoz Chemical Co., Ltd., Messrs Durand & Huguenin S.A., Messrs Bard & Wishart, and The British Ultramarine Manufacturing Co., Ltd., *per* Mr T. Saville Whittle, the author is specially indebted for the preparation and supply of the patterns required to illustrate the book, and for placing at his disposal valuable technical data relating to methods of production—data of which ample use has been made. He also desires to express his sincere thanks to Messrs Mather & Platt, Ltd., for numerous illustrations of plant employed in the industry, and, in particular, to their representative, Mr F. B. Dixon, for his suggestions and his kindness in arranging for special blocks to be made to suit the format of the book. He desires further to record his warmest thanks to Dr Richard Fischer (I. G. Farbenindustrie), Mr H. B. Briggs (Imperial Chemical Industries), Dr G. Tagliani (Sandoz), Dr Muller (Geigy), and other (anonymous) chemists in all the aforementioned firms, for the invaluable assistance they have rendered in supervising the actual execution of the printed patterns; to Mr G. Holland Ellis and the British Celanese Co., Ltd., for information on the printing of Celanese goods; and to Messrs Alfred Edge, W. G. Dixon, J. Nuttall, D. S. Naylor, J. Wishart, A. Williams, and B. Davenport, for much useful help on questions concerning recent developments in colouring matters and processes. The author hopes that all these gentlemen and their respective firms will accept, once and for all, the expression of his heartiest appreciation of the aid he has derived from them, and his sincere thanks for the help which they have given with such unfailing courtesy and goodwill.

In conclusion, the author trusts that the present edition will meet with the same cordial reception as did its predecessors, and that it will prove equally acceptable and useful to those engaged in the industry.

J. B. FOTHERGILL.

MIDDLETON, *April* 1936.

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ABBREVIATIONS.—The letters in brackets represent the initials of firms to whom the authors are indebted for the patterns in the following list. C.P.A. = The Calico Printers' Association, Ltd.; I.C.I. = Imperial Chemical Industries, Ltd.; H. & C. = Horridge & Cornall, Ltd.; S.C.I.B. = Society of Chemical Industry, Bâle; I.G. = Interessen Gemeinschaft für Farbenindustrie, Frankfurt a./Main; D. & H. = Durand, Huguenin & Co., Bâle.

Calicoes.

PART I.

INTRODUCTION.

INTRODUCTION.

THE term "textile printing" is used to signify the production, by various means, of coloured patterns or designs upon all sorts of textile fabrics—cotton, wool, silk, jute, linen, and various mixtures of these and other fibres.

Textile printing is really a form of dyeing, but differs from that art in that the cloth, instead of being uniformly coloured throughout by immersion in a solution of dyestuff, has one or more thickened colours or mordants applied to it locally, the colour being developed by steaming, etc., or by dyeing. The close relationship existing, however, between the two is emphasised by the fact that although it is quite possible to print on cloth almost any form of colour capable of being converted into a viscous fluid—as, for example, paint, coloured wax, etc.—yet, broadly speaking, the whole of the colouring matters employed in the one industry are identical with those employed in the other.

HISTORICAL.

The beginnings of the art of ornamenting textile fabrics by the stamping or printing on of coloured designs are lost in antiquity. They are usually assumed to have originated in the Far East, where the Hindoos and Chinese are known to have practised hand printing with wood blocks from the earliest times, but recent discoveries in the Pyramids, and other Egyptian tombs, of fragments of cloth undoubtedly decorated by some process other than dyeing alone prove pretty conclusively that the ancient Egyptians also were acquainted with some form of the art. Textile printing was also practised by the Peruvians before the Spanish conquest in 1531–1532, but whether they discovered the process for themselves or derived their knowledge of it from outside sources (which is not likely, considering the limited means of communication they possessed at that date) is not known. Taken altogether, then, it is probable that the art of printing on textile fabrics was discovered independently and at different times by each of these nations.

On historical grounds, it would appear that the Chinese and Hindoos are about equally justified in claiming credit for the invention of *block printing*; for, while Pliny the Elder (A.D. 23 to A.D. 79) certainly alludes to some unknown process whereby the Egyptians of his time produced patterns on dyed cloth, it is on record that letterpress printing from *engraved wood blocks* was extensively practised in China nearly two thousand years ago, and, further, that valuable Indian fabrics *printed in colours* were known to, and esteemed by, the Romans in the days of the Empire. From this latter circumstance, which shows that the Hindoos had already gained a world-wide reputation for the excellence of their printed cottons, it may, not unreasonably, be inferred (*a*) that block printing, even at this early date, was an old-established industry in India; and (*b*) that any contemporary work produced in Egypt was either not executed by the process used by the Hindoos, or was still in the experimental stage, from

which it seems never thoroughly to have emerged. Leaving, therefore, the Peruvians out of the discussion—for no information relating to their work is available earlier than 1532—the question of the priority of discovery is narrowed down to the consideration of the rival claims of China and India. If we except the Assyrians, who employed carved wooden stamps for impressing cuneiform symbols on wet clay tablets and bricks, the Chinese, so far as is known, were the first to make use of engraved wood blocks for any kind of real printing. It is not unlikely, therefore, that they were the original discoverers of calico printing, for it is quite possible that the idea which led up to their invention of letterpress printing would suggest the feasibility of applying the same process to the ornamentation of textiles. That they produced block-printed fabrics in very remote times is unquestionable, but whether or not they anticipated the Hindoos in this respect is still a matter of conjecture, and even now, after a century or more of controversy, appears to be as far from settlement as ever. In fact, the rival claims of China and India to the honour of priority are based upon pure circumstantial evidence alone. Without going into detail, it may be interesting to note the main line of argument followed in each case.

Taking China first :—In the absence of direct proof to the contrary, it has been postulated by those who hold that textile printing originated in China, that because the Chinese were the first to practise letterpress printing, they would naturally be the first also to practise textile printing. This plausible argument, which depends entirely, for any value it may possess, upon the assumption that the highly civilised, ingenious, and technically skilful Chinese *would be certain to recognise almost immediately* the possibility of applying the principle of their newly invented letterpress process to the decoration of textiles, is pertinent enough to account in some measure for the rise of textile printing in China ; but, as a factor in the determination of the probable *date* of that rise, it loses most of, if not all, its specious importance when submitted to analysis. Considering, for instance, that letterpress printing and dyeing are two very different crafts, with nothing in common ; that in early times, in China, each craft was a " mystery," the processes of which were only known to and practised by those who had been duly initiated ; and that, until comparatively recently, all new discoveries and methods were jealously guarded and kept secret as long as possible, it is in the highest degree improbable that —in the days when letterpress printing was a new invention, and dyeing a purely empirical process—either Chinese printers or dyers would know anything of the technicalities of each other's crafts ; or, at least, would be sufficiently conversant with their practice to realise at once the possibility of combining them for the purpose of producing decorative effects hitherto unknown on textiles. In that unscientific age the development of an industry was necessarily a very slow process, and it is not unreasonable to suppose, therefore, that a considerable interval of time elapsed between the introduction of letterpress printing and that of textile printing ; for, on the one hand, the printers, for a long time, would naturally confine themselves to, and be fully occupied in, perfecting and working their own particular invention, while, on the other hand, the contemporary dyers, following their occupation on " rule of thumb " lines, would be scarcely likely to conceive *at once* the idea of extending the scope of their craft by the application of an entirely new invention (the object, appliances, processes, and materials of which were so totally different from anything to which they were accustomed), especially as no mode or style of textile decoration then existed capable of giving them a lead in that direction. In any case, the assumption that the invention of letterpress printing involved that of textile printing, and that the two were practically coeval, is nothing more than a mere conjecture, based on possibilities which, though plausible

enough on the surface, are found to be rather too subtle and too remote to be unhesitatingly accepted as probabilities when contrasted with the actual course along which the development of letterpress and woodcut printing proceeded in Europe during the Renaissance. To trace the successive steps in this development is both needless and beyond the scope of the present work; but it may be noted that, although block printing was extensively employed in the fifteenth, sixteenth, and seventeenth centuries for the ornamentation and illustration of books and for the reproduction of works of art, it never suggested itself to the printers and dyers of those times as suitable for general application to the ornamentation of textiles.

It thus appears that block printing *on paper* was not so inherently suggestive of textile printing as some seem to have imagined. Had it been so, it is inconceivable that such an important feature, which is assumed. for the purposes of argument, to have been patent to the early Chinese, should have escaped entirely, in analogous circumstances, the keen observation of mighty minds like Albrecht Dürer, Hans Holbein, Lucas van Leyden, and all the other great exponents of wood engraving; and that, too, in an age when craftsmen were no less expert, no less ingenious, no less civilised, and, if anything, more alert to seize upon any means of extending their trade, than were the Chinese of fifteen hundred years before. On the whole, then, while granting that the relationship between the two processes is sufficiently close to afford a certain amount of presumptive evidence in support of the view that textile printing in China was derived, in the first instance, from letterpress printing, it cannot be said that any real grounds exist for the broad assumption that their respective inventions were coeval, and consequently it is safer not to assign the invention of the former (in China) to any definite period.

Secondly, as regards India:—Unfortunately, up to the present, no record has been discovered indicating, in the slightest degree, the approximate date at which block printing was first practised in India. But the simple fact of the beginnings of an industry, common to two countries, being put on record in the one and allowed to pass unnoticed in the other, is not of itself any proof that that industry was originated in the first, or that it was introduced into the second from outside. Other considerations must be taken into account before the evidential value of a mere record can be properly estimated; and so, curiously enough, in the case of India, the lack of historical data relating to the rise of textile printing, so far from prejudicing the Hindoo claim to priority in invention, tends rather to substantiate it. In this connection the following points are especially worthy of notice:—

(1) During the period in which textile printing is supposed to have been invented in China, the government of India was in the hands of the Brahmins, who, besides being the priests, scientists, philosophers, and lawgivers, were also the actual administrators of the country, and the sole custodians and interpreters of the Vedas—a series of Sanskrit writings revered as sacred by the Hindoos. According to the Vedic story, which was invented about 1200 B.C. by the Brahmins to justify their own claims to power, "Brahma—the Creator of all the World"—created four classes or "castes" of men from his own body, namely, from his head the *Brahmins*; from his arms the *Kshatriyas* (warriors); from his thighs the *Vaisyars* (tradesmen, craftsmen, and farmers); and from his feet the *Sudras* (menials). Further, it declares that the Veda was miraculously produced from Brahma's mouth at the same time as the Brahmins; that it was to be committed to their charge alone; and that it was to be taught and expounded by them only. Thus invested with divine authority, the Brahmins were regarded as beings of peculiar sanctity, and were held in high honour throughout India. In order to maintain their social, political, and religious supremacy,

they adopted the policy of attributing the origin of every branch of art, science, and manufacture to the Veda, adding to it as they thought fit. They instituted the laws of Manu which not only defined exactly the social and religious status of each caste, but regulated everything relating to the daily life of its members —food, clothing, occupation, education, and marriage,—and severe penalties were exacted for the slightest violation of their stringent ordinances. Moreover, they compiled a series of works, known as the Sutras, which, although not asserted to have been directly inspired by the god Brahma himself, were alleged to be based upon the sacred Vedas, and consequently had divine sanction for the statements they contained. In these Sutras they not merely elaborated their religious system, but insisted upon the recognition of their claim to be considered as a sacred, independent, and superior caste, supreme alike over kings, princes, and people.

By these and other means the Brahmins, little by little, extended their sphere of influence, and gradually, but not without some opposition, succeeded in forming practically the whole mass of the mixed population of India into one great social and religious Brahminical organisation—Hindooism—with themselves as its acknowledged leaders and sole directors. Notwithstanding the fact that Buddhism was in the ascendant from about 200 B.C. to 600 A.D., the Brahmins never lost their prestige, nor relinquished their policy of ascribing all new knowledge to the Vedas, for which purpose they kept themselves *au fait* with current developments in all branches of work that they considered of any importance. Neither did they cease from advocating a return to their own particular tenets, which were never entirely superseded by those of Buddha; and as they (the Brahmins) still retained the monopoly of Vedic learning, and were by far the most highly educated section of the Hindoo population, they continued to exercise considerable influence throughout the whole of the above period upon the secular affairs of the people, in whose minds the idea of caste was too firmly rooted to be easily eradicated, by a new and wholly ethical religious system, the central principle of which was that future well-being could only be obtained by those who lived a virtuous and charitable life on earth. To a people steeped in ignorance and superstition, such a doctrine was both incomprehensible and much less acceptable than the Brahminical teaching of expiation by propitiatory sacrifices to the gods—an easy way of atonement, and one which afforded a sense of comfort to those who believed in its efficacy. Again, the restrictions placed by Buddha upon indulgence in pleasure, and the observance of the moral precepts he enjoined, proved in practice too rigid and austere to find favour with the mass of the people, and consequently, although Buddhism was nominally the chief religion for about a thousand years, it never displaced Brahminism in any considerable part of India. The two religions were coexistent during the whole of this time, and about equally popular, in many instances flourishing side by side in the same district.

In its highest form, Buddhism was essentially a religion for the devout few. The ideal of Buddha was too lofty and his rules of life too strict for wholehearted acceptance by the rank and file of the people of his time, and after his death his teaching was, little by little, incorporated with a mass of pagan legend and superstition, until it finally became transformed into a system of idolatry, pure and simple, with Buddha as god. The priests, instead of living the poor, simple, and humble lives ordained for them by Buddha, became rich, luxurious, exacting, and arrogant, and this, together with the debased condition of Buddhism generally, probably contributed in no small measure to the retention by the Brahmins of their old-established temporal power.

(2) If, therefore, textile printing was brought into India from China, it is incredible that its introduction, as a *new foreign industry*, should have escaped

the notice of the Brahmins, whose policy, as previously mentioned, was to assign the origin of all knowledge to the Vedas, and through them to Brahma. Even granting that its first entry into the country may have been unobserved by the Brahmins, it is almost impossible that the sudden appearance of the entirely novel decorative effects obtained by its means could have failed to attract their attention and to excite their curiosity; so that, in any case, if textile printing really were of foreign origin, it is surprising that, so far as is known, no attempt was made in the Brahminical writings to attribute its inception to the Vedas.

(3) If, on the other hand, it be considered as an invention of the Hindoo dyers themselves, the absence of all historical evidence relating to its commencement in India is, in one way at least, easily explainable. For in this case the Brahmins would probably regard printing as a mere modification or a branch of the already old-established art of dyeing, and, as such, of too little importance to merit separate mention. Dyeing being one of the industries carried on by the lower castes (Vaisyars and Sudras), was, naturally, not at all interesting *technically* to the Brahmins, and consequently any improvements made in its methods and processes would not be likely to come under their notice, especially if they were effected gradually, as must have been the case with textile printing.

Apart from all questions of evidence or surmise, the fact that textile printing was an extensive and highly flourishing industry in India during the earliest centuries of the Christian era is of itself almost sufficient to dissipate the notion that the art was introduced from China. In view of the reasons already adduced for supposing that the development of textile printing in China proceeded at the usual slow rate of all ancient industries, it is probable that the earliest date at which it could possibly have been introduced into India approximated fairly closely to that at which the products of Hindoo block printers were already known and appreciated in imperial Rome—a fact which clearly demonstrates that even at that early date the industry in India was not merely firmly established, but was established on a more or less extensive commercial scale. Taken altogether, then, it would appear that the most reasonable conclusion to draw is, that textile printing in India was a native invention, and that its advanced state of development, and the high estimation in which Indian calico prints were held at the beginning of our own era, were the result, not of any improvements that may have been effected by the Hindoos in a comparatively recently imported foreign industry, but of their long practical experience of an indigenous craft—an experience probably extending backwards, through many generations, to a period long anterior to that at which letterpress printing was first practised in China.

It is quite possible, therefore, that the Chinese derived their knowledge of block printing from the Hindoos, instead of the reverse being the case, as is frequently argued. In this connection, however, nothing can be positively affirmed; and it is well to remember that, judging by the development of other industries, similar materials and methods would not be at all unlikely to suggest themselves as suitable for the decoration of textile fabrics, to dyers, quite independently, in countries and times widely separated.

Textile printing in Europe presents a similar problem—its actual beginnings are equally obscure. According to R. Forren (*Die Kunst des Zeugdrucks*, 1898) it originated in the Middle Ages and was carried on, during several centuries, in various Rhenish monasteries and in their immediate neighbourhood. That some elementary form of the industry was practised in these monasteries at a period very much earlier than is generally supposed is sufficiently established by the existence of fragments of their productions that have come down to

us from mediæval times—fragments of block-printed linen and silk, of which some examples, in the Victoria and Albert Museum, and in the museums of Paris and elsewhere, are known to date back to the fourteenth century, while others are even attributed to the twelfth and thirteenth centuries. It would thus appear that, in Europe at least, textile printing preceded letterpress printing, for Gutenberg, the reputed inventor of the latter, was only born about 1400. Beyond the fact that the old monks used blocks for printing, nothing is known of the processes they employed. In all probability they made use of the ordinary pigment colours mixed with oil, for at that period the knowledge of mordants and dyestuffs in Europe was not such as could be applied to the production of *dyed* prints. Whether they themselves discovered the methods of printing, or whether they derived their knowledge of them from outside sources, is not known. Possibly full credit is due to them for the invention. On the other hand it may be that they developed the process in attempts to imitate Eastern fabrics imported from the Levant by Venetian merchants; or, again, it may have been introduced by some member of their order who had travelled in the East and seen textile printing in operation. No record exists to lend support to any of these alternatives, and at this distance of time it is impossible to say how much of their work was original or how much was borrowed. One point, however, is worthy of note in this connection, viz. that if their productions were inspired by examples of Eastern work, it is remarkable that they bear so little resemblance to any contemporary Indian, Persian, or Coptic prints. The old Rhenish printers turned out well-planned Gothic and Byzantine patterns, which, judging from their scale, were intended for decorative purposes rather than for personal use. Had they worked with Eastern examples before them they could scarcely have escaped, so entirely, betraying some influence of Eastern design in their own manufactures—an influence exerted so powerfully in later times. Hence one is tempted to think that perhaps Europe is not quite so much indebted to the East for its textile decoration as has been hitherto supposed.

The industry was never very extensive, and, after the fourteenth century, it gradually declined, until finally it became extinct, and was forgotten so completely that it may be said to have had no influence on the development of the modern industry.

The source of modern European textile printing can be traced, easily and directly, to India; and, consequently, so far as Europe is concerned, India is undoubtedly the true birthplace of the modern industry. From India it spread slowly westward, by land, through Persia, Asia Minor, and the Levant, until it finally reached Germany, France, and England, towards the latter part of the seventeenth century. At about the same time, French trading vessels brought samples of Indian prints, together with full particulars of their manufacture, direct by sea, from the French possessions on the east coast of India, and probably, therefore, the French were the first to practise calico printing in Europe. If so, the art very rapidly became known in Germany, for towards the close of the seventeenth century Augsburg was celebrated throughout the Continent for the excellence of its printed linens. The first attempts to imitate Indian chintzes are, however, believed to have been made in Holland, where the Dutch East India Company introduced printed calicoes before they became generally known in France and England. Some support is lent to this view by the fact that certain authorities attribute the introduction of textile printing into England to Flemish workmen in 1676; but it is very uncertain as to where, when, and by whom the first attempts really were made, and it is probable that they took the form of painting rather than that of printing. Thompson of Clitheroe, an expert calico printer, and one of the greatest

authorities of his time on the subject in all its bearings, assigns the beginning of the art in England to a somewhat later date, and asserts that we owe our knowledge of textile printing to a French refugee who established the first printworks *on record* at Richmond-on-Thames in 1690. It would appear, however, that some process of printing or ornamenting textile fabrics was already carried on in this country prior to this date, for, in a pamphlet published in 1677, Sir Joshua Child refers to cotton cloth imported from India for the express purpose of being printed in England in imitation of Indian chintz patterns. A patent taken out in 1619 shows that even at that early date Indian printed calicoes were known in England; and a petition presented to Parliament in 1627 bears evidence to the fact that their importation had by that time become sufficiently important to threaten the interests of English textile workers. The East India Company, however, was too powerful for its opponents, and in 1631 printed calicoes were scheduled, subject to an import duty, as legal articles of commerce. From this time forth English manufacturers sought to restrict their importation by (1) agitating for an increase in the duties, and (2) by doing their best to put competitive imitations on the market. In both of these objects they were eventually successful; but some of the earlier patents show how ignorant they were of the method, and how far letterpress printing failed to suggest to them the true principles of block printing on textiles. For instance, in 1634, a patent was granted for a process of applying patterns cut out in silk, wool, and other fabrics to cotton cloth, affixing them thereto by means of oil, gums, and other adhesives. Other patents dealt with methods of painting on dyestuffs and pigments, but none of them seems to have been successful in practice, and after 1690 block printing replaced them all. In 1689 a printworks was established at Neuchâtel by Jacques Deluze. The reputation attained by this works stimulated other countries to follow suit, and in a short time calico printing had spread rapidly in France, Germany, England, and Portugal, and was greatly extended in the Netherlands, which have always been celebrated for the imitation of "batticks," a style of decoration peculiar to Java and the East Indies generally.

After the closing of the Richmond Works by the death or return of its founder, a printworks was started at Bromley Hall, in Essex, and subsequently others were established in Surrey, to supply the demands of the London market.

Calico printing was first practised in Scotland in 1738, and twenty-six years later was introduced into Lancashire, where, in 1764, Messrs Clayton, of Bamber Bridge, near Preston, laid the foundations of what has since become one of the most important industries of the country.

Block printing being only suitable for comparatively coarse designs, Bell, a Scotchman, conceived the idea of printing calico in the same way that engravings are printed, viz. from engraved copper plates. This process was largely employed in London for many years; but technical difficulties in the way of making the successive impressions join up imperceptibly limited its application to certain styles of pattern, such as those suitable for handkerchiefs and designs made up of detached objects. These shortcomings were entirely overcome in 1783 by Bell's invention of the roller or cylinder printing machine—a machine which was not only capable of being applied to almost every known style of design, but revolutionised the industry by enabling large quantities to be produced at a cheap rate, thus bringing printed calicoes within the reach of the million, upon whose consumption alone depends the success of any great industry.

Oberkampf, of Jouy-en-Josas, was the first to introduce the roller machine into France, and he made such excellent use of it that for a long time he was looked upon by the French as its inventor. Bell's claim is now, however,

generally admitted, for as the machine was unknown to Oberkampf before 1800, and was working in England in 1785, it stands to reason that it could not have been invented by the French printer.

With the exception of a few refinements of movement, and a few additions extending its range of usefulness, the machine in use at the present day is substantially the same as that invented by Bell one hundred and fifty years ago—a fact which shows how successfully he overcame all the difficulties of the problem he set himself to solve.

But improvements in calico printing were by no means confined to the mechanical methods of its application; many processes were improved and new ones invented, and many new colours were gradually added to the palette, so to speak, of the calico printer's colourist.

Down to about the end of the eighteenth century dyers and printers were almost entirely restricted to the use of vegetable dyestuffs, especially in patterns containing several colours; but with the advance of chemical science all but the best of such colours have been replaced by artificial products. Amongst the earliest improvements in this direction may be mentioned the employment of mineral colours developed on the fibre—Iron buff, Prussian blue, Antimony orange, Manganese bronze, and the yellow and orange chromates of lead. The year 1856 marked the beginning of a new epoch in calico printing, for in that year W. H. Perkin opened up a new and vast field of chemical research by his great discovery of "Mauve"—a colouring matter derived from that apparently most unpromising material, coal-tar. Following the lead given by Perkin, Medlock prepared Magenta in 1860, Griess the diazo-compounds in 1864, and Graebe and Liebermann a method of producing artificial Alizarin, the essential colouring principle of madder root, in 1868. Synthetic Indigo was prepared by Bayer in 1897, and, as far as calico printing is concerned, it has entirely replaced the natural product, being specially suited for this purpose on account of its freedom from sand and other gritty particles, an advantage which ensures better and more regular results, besides effecting considerable economy in other directions.

The resources of the calico printer and dyer are constantly added to by the unceasing production of new and improved artificial dyestuffs, and the number at his disposal is now so enormous and their properties so diverse that he is enabled to introduce almost any shade demanded into styles of work that were formerly restricted to one or two colours only.

At present calico printing is carried on in almost every civilised state in the world, and its advance during the last two centuries has been so stupendous that the combined annual output of the numerous works is now, probably, many times greater than the sum-total of the production during the whole of the eighteen centuries preceding the invention of Bell's roller printing machine.

GENERAL CONSIDERATIONS.

A piece of printed calico is at once one of the most familiar, most useful, and perhaps the most wonderful of all the wonderful products resulting from the practical application of human ingenuity to the service of man. The decorative purposes to which printed goods can be put are so numerous and varied, and the needs they supply so universal and diverse, that they have become a household requisite in every class of society, and are so widely disseminated that a "bit of print" is now to be found in almost every palace, cottage, hut, and tent of every country with which commercial relations have been established.

In *first-rate* modern calico prints beauty and utility are united, and the result represents, to a degree hitherto unapproached by any other article of

domestic use, the combination of some of the most splendid achievements of mechanical genius, scientific research, and artistic skill. And yet, despite all this, even the finest of these fine examples of applied science and art evoke but little real interest, and are nowadays looked upon by the public as very commonplace things indeed. The wealth of thought, expert knowledge, and skilled labour brought to bear upon their production (not to mention the vast expenditure entailed, and the imposing, yet delicate and exact, machinery employed) is only equalled by the stolid, matter-of-fact indifference with which the result is regarded. It is true that printed goods are immensely popular, but their popularity is independent of any artistic merit they possess, and is due rather to their affording a cheap, clean, and convenient means of introducing *colour* and *pattern* into the wardrobe and the decoration of the home, than to the facts that they are the outcome of centuries of experiment, and the concrete realisation of the devoted study of generations of artists, chemists, and engineers. To the great majority of purchasers a calico print is purely and simply a calico print—pretty, maybe, and useful, but beyond that nothing more than a piece of coloured cotton, a thing of little value and of less interest; and it rarely or never occurs to them that any process at all is involved in its production. Perhaps this is not to be wondered at, for the very abundance and the cheapness of printed fabrics have brought them within the reach of all, even the poorest; and now that they are common objects in every household, they are no longer novelties, and have ceased to attract any particular attention. In short, if familiarity has not exactly bred contempt, it has at least bred apathy; and yet, if the purchaser were only able to realise that in high-class calico printing many of our most talented designers find almost constant employment for their inventive faculties in the creation of new and artistic patterns, and that their ideas are, more or less, adequately expressed in practical form through the medium of the most perfect application of the latest discoveries in tinctorial chemistry and the most recent improvements in machinery, he would appraise the result at a very much higher figure than its price per yard, and would probably find that a calico print of the best quality possessed artistic merit and scientific interest far beyond what he had imagined.

Although calico printing, on an industrial scale, is not perhaps the form of applied art best suited to display the individuality of any one man, it is nevertheless capable of yielding results the artistic and decorative qualities of which entitle it to a prominent place in the ranks of those influences which make for true beauty in our immediate surroundings. The ingenuity of the artist and chemist has a scope in calico printing such as is afforded by no other industry devoted to the decoration of textiles. The vast variety of effects obtainable—ranging from the most bewildering intricacy of fine pattern and the utmost delicacy of ornament, to the broadest effects of heavy line and mass,—the possibility of presenting the same pattern in numerous and diverse combinations of rich permanent colours, and the adaptability of the process to ornament of every style and to fabrics of every kind, give a freedom to fancy and an impulse to originality in the selection and treatment of suitable ornamental material that are not to be found in any other direction. With its wide range of possibilities, calico printing affords the chemist almost unlimited opportunities for introducing new, improved, and elegant effects of all descriptions, and offers to the designer, amongst other things, a means of conveying to the masses, for whom he largely works, new, clear, and truthful impressions of many of the subtler features of plant forms which are too delicate for reproduction by any other method of textile decoration. The result is that, at the present time, a collection of the best examples of the work of the best calico printing firms exhibits fertility of invention, beauty of form and colour, wealth and variety

of incident, and a rare discriminative faculty in the selection of just those features of natural plants best suited to the work in hand, and in their adaptation to the embellishment of the fabric in question—all of which qualities stamp the goods which possess them as artistic productions. Of course, no one would contend for a moment that calico printing can equal the richness of either tapestry or silk-weaving, in both of which crafts the variety of surface obtainable, and the texture and lustrous sheen of the materials employed, add considerably to the resources of the designer, and impart to the work a beauty quite distinct from that of its pattern and colour alone; but for cheaper work, within the reach of everybody, calico printing offers a ready and reliable means of producing pleasing coloured patterns on a variety of fabrics—patterns which, from an artistic point of view, leave nothing to be desired, and in many cases are superior in artistic merit to those commonly employed for even the most costly and sumptuous goods in woven wool and silk.

A *first-rate* example of calico printing is, therefore, worthy of much more consideration than it usually receives, and, so far from being a mere commonplace article, it is "a thing of beauty," and if not exactly a "joy for ever," is at least, so long as it lasts, a source of pleasure to those who can intelligently appreciate its excellences. Unfortunately a vast amount of modern machine-printed work, although perfectly executed, is undoubtedly artistically bad, inasmuch as the facilities of the process have been grossly misapplied in stupid and nugatory attempts to imitate deceptively the conventional treatments of ornament peculiar to, only suitable for, and characteristic of quite other methods of textile decoration. Printed imitations of woven "effects"—embroidery, patchwork, appliqué, lace work, tapestry and chenille hangings, etc.—are artistic barbarisms, whose only claims to notice are (1) that they exemplify what ought to be avoided in calico printing design; (2) that they are typical of what consummate technique, unrestrained by a sense of fitness, is capable of perpetrating in way of catch-pennies; and (3) that they seriously hamper a rightful appreciation of better work, in that those who purchase them (and there are thousands who do) have the impression that their superb execution must needs, in some unexplained way, imply equally superb design. To a cultivated eye, however, such productions represent the acme of perverted taste; and as they are palpably the work of the mere slavish imitator, ignorant, or wilfully disregardful, of the wonderful artistic possibilities of his craft, they scarcely merit more than mention and dismissal. The same remarks apply to those attempts at the literal transcription of Nature which are made to do duty as designs in so many of our modern cretonnes. They, too, are imitations —pretentious imitations—all the more to be deprecated because they convey entirely erroneous impressions of what they are supposed to represent, namely, the actual appearance and habits of growth of natural plants. Moreover, they are obviously inconsistent in treatment, some parts of them being naturalesque and others conventional. This cannot, of course, be avoided; for the conditions of calico printing absolutely require the pattern to repeat itself exactly at frequent and regular intervals; and consequently, while it is possible to imitate deceptively certain parts of a plant or flower, it is altogether impossible to represent its natural appearance as a whole, for Nature never repeats herself. Realistic or naturalistic design involves no effort of the imagination, and requires no more invention than is entailed in twisting about ready-made ornament until it fits a given space without leaving unsightly gaps. Natural flowers, if well drawn, may be an *adornment*, but they are certainly not *ornament* in the proper sense of the word, for, strictly speaking, pure ornament implies, not the servile copying of Nature, but the adaptation of modified natural forms to the enhancement of useful articles. The modifica-

tions or changes which are effected in natural forms during their transformation into ornament constitute what is known as conventional treatment; and as each material and method employed in the applied arts possesses characteristic qualities and distinctive limitations, which must (in practice) be taken into account in designing for it, this conventional treatment takes various forms according to the circumstances under which it is to be applied. It follows, therefore, that no definite rules can be formulated as to the extent to which the process of conventionalisation may be safely carried: it is largely a matter of good taste, guided and controlled by constant reference to Nature, and to the conditions of execution or manufacture. Without going into the subject of design, which is beyond the scope of the present work, and will only be touched upon lightly in the following pages where required to explain certain technical necessities, it may be said that conventionalisation consists (1) in simplifying, emphasising, or exaggerating the salient features of natural forms so that their ornamental significance is perfectly clear; (2) in arranging them on definite lines, thus reducing their waywardness to order; and (3) in so treating them that their luxuriousness and infinite variety are capable of being expressed in the easiest, most rational, most suggestive, and most effective way in the material and by the process for which they are designed. To do this properly demands much more of the designer than a well-trained eye and consummate draughtsmanship. Both are necessary to him; but if he is to originate anything new, he must, in addition, be a profound student of Nature and of the history of his art; must learn to understand that natural forms, while eminently adapted to Nature's purposes, are unsuited to the very different purposes of ornament; he must further possess the rare faculty of selecting, and restricting himself to, just those natural features best suited to the work he is engaged upon; and he must be sufficiently conversant with the capabilities and peculiarities of the materials and processes with which he has to deal to enable him, by appropriateness of treatment, in conjunction with an artistic perception of colour and form, to utilise their characteristic qualities to the utmost advantage, and at the same time to keep well within their limitations. Other things being equal, the degree to which the possibilities and limitations of material and means are honestly recognised and respected by a designer is a measure of his technical proficiency and of his power of interpreting Nature in the best possible way; for only by a wholesome and intelligent appreciation of the influence of material upon design can he hope to add to the beauties of form and colour in his work, that "beauty of fitness" which is an absolutely essential element in all decorative work that claims to be artistic. To attempt to get more out of materials and processes than they are naturally capable of expressing is to repudiate their characteristic qualities, and, consequently, to depreciate the value of and to enfeeble the resulting work by depriving it of, perhaps, its greatest charm, viz. the evidence that it ought to bear to its ornament having been designed with direct reference to the conditions of its execution. In calico printing, as in all applied arts, technique governs design. To one sufficiently acquainted with the capabilities of the various methods of printing, it suggests in no uncertain manner the most appropriate treatment and the best kind of conventionality to adopt in a given case, and its limitations, so far from restricting the play of a clever designer's fancy, and slackening his invention thereby, are an incentive to further effort, and become in his hands sources of fresh beauty.

This brief review of some of the more important *general* principles underlying all good design whatsoever will give the reader some idea of the vital necessity of adapting design to process, and may perhaps help him to realise that a well-designed, well-executed calico print is not merely a useful article, but one

capable of appealing to the most refined taste in matters artistic, and full of interest to the scientist, and to the craftsman and designer, who, whilst naturally finding their chief delight in certain superior qualities of the best hand-printed work, are yet sufficiently broad-minded to appreciate fully the value of the enormous resources placed at their disposal by modern machinery and methods.

Of many calico printing firms, both at home and abroad, it can be said with truth that in their best work they apply perfectly the true principles of ornament, and, by calling in the aid of the best artist-designers who thoroughly understand the exigencies of manufacture, and by carefully avoiding the meretricious imitative and naturalistic effects which brought about the decadence of calico printing in the nineteenth century prior to the advent of William Morris, they succeed in producing work of artistic distinction and fitness ; work which ought to become—and will become when its merits are more generally recognised and acknowledged—an important factor in educating the public to a fuller appreciation of all that is best in applied art.

A first-rate calico print, apart from its useful and decorative qualities, and its charm as an expression of human thought and invention, is a wonderful example of what can be achieved when art, science, and commerce work harmoniously together, and it illustrates very aptly one of the most important chapters in the history of our industrial development. It brings many and varied activities to a focus ; and, whether the result of their co-operation prove artistically pleasing or otherwise, no one, except the grossly ignorant, can, after a moment's consideration, honestly describe it as either inartistic, uninteresting, or commonplace.

PART II.

METHODS OF PRINTING.

METHODS OF PRINTING.

APART from weaving, embroidery, painting, and appliqué, etc., there are five distinct methods of producing coloured patterns or designs on various textile fabrics :—

(1) By hand block printing.
(2) By perrotine or machine block printing.
(3) By stencilling.
(4) By flat-press printing from engraved copper plates.
(5) By machine or cylinder printing from engraved copper rollers.

Of these five methods, cylinder printing is by far the most important ; but hand block printing is coming more and more into use again for certain styles of work, and the perrotine machine, although little used in England, still finds extensive and increasing employment on the Continent. Stencilling has up to the present found but little application on a large scale, and flat-press printing on textiles is practically obsolete except in Switzerland, where it is used to a slight extent, in conjunction with block printing, for the production of a special class of work. Occasionally machine or cylinder printed goods are filled in by hand block printing—notably in the case of certain brightly coloured handkerchiefs for the East, in which the red ground is printed by machine, and the brilliant pinks, yellows, blues, and greens are subsequently " put in " by hand printing ; and it is quite possible that very fine decorative effects could be obtained on canvas and jute by combining block printing with stencilling, as is already done in coloured woodcuts and for friezes.

Each of the above five methods of printing possesses inherent advantages as well as disadvantages, so that no single one of them can either replace or be replaced by any of the other four without sacrificing some desirable and characteristic quality in the resulting work. The discussion of the æsthetic value of these various characteristic qualities does not fall within the purview of this book ; but as they are functions of process, they determine, to a great extent, the choice of the particular method to be adopted for the execution of a given design, and consequently some mention must be made of their influence in practice, and of the causes from which they arise, in order to convey an adequate idea of the scope of the several methods of calico printing.

In the following descriptions, therefore, they will be dealt with from a strictly practical point of view, and as briefly as is consistent with a proper explanation of the points they are intended to illustrate.

(1) BLOCK PRINTING BY HAND.

The art or craft of block printing consists in cutting a design in relief upon blocks of wood, so that the raised parts when charged with colour will transfer the design to whatever fabric the block is stamped upon. It is the oldest, and generally considered to be the most artistic, of all methods of printing textiles, but it is a slow and somewhat expensive process, and is, moreover, in its prac-

tical application, more strictly limited to certain styles of design than is its modern competitor, the cylinder printing machine.

The subtle gradations of tint and stipple, the delicate cross-hatchings, the fine, sharp outlines, the clean cut edges of the masses, and the absolutely invisible joining-up of the repeats of even the smallest "cover" patterns—all features so characteristic of most designs printed by the cylinder machine—are altogether impossible to obtain by block printing of any kind.

On the other hand, a first-rate block print, whatever it may lack in mere mechanical neatness, is unsurpassed for its breadth of effect, its decorative value, its freedom from finicking detail and elaborate shading, and, above all, for the purity, richness, and transparent quality of its colour, which, in large masses, has the pleasing appearance of a water-colour wash. Compared, too, with perrotine, flat-press, and stencil printing, block printing by hand possesses many advantages. The perrotine is only capable of being applied to designs small in scale and containing not more than three colours; on the flat-press, continuous patterns are impracticable, and it is most difficult to print more than a single colour. By stencilling, unbroken outlines cannot be obtained except by exceeding the proper and natural limits of the process; but by hand block printing, patterns containing any number of colours and on any scale can be reproduced with ease and certainty, the only condition of success being that their ornament must be treated in a broadly conventional manner.

On the whole, then, hand block printing is, *after cylinder printing*, the most generally applicable, and, in consequence, the most important of all other methods, so much so in fact that cylinder printing is its only rival, and that solely in certain classes of work where mechanical precision is a feature of the design, or where cheapness (but not necessarily vulgarity) is a desideratum.

The principles of block printing differ entirely from those of cylinder printing, and it is to this difference that the distinctive character of the work produced by block is to be attributed. If, therefore, the fullest advantage is to be taken of the best qualities of either method, it is evident that the proposed design must be drawn up with due regard to the possibilities and limitations of the particular method which is selected for its reproduction. These possibilities and limitations arise from the nature of the processes and materials employed, and, so far as the two methods in question are concerned, their influence on design is best explained by comparing the fundamental principles of engraving, and of printing from, wood blocks and copper rollers respectively.

In wood engraving—or "block cutting," as it is termed technically—the design is cut or otherwise raised in *relief* on a thick, *flat* block of wood; colour is then applied to the *raised parts*, and the impression of the design obtained by stamping the block smartly by hand on the cloth to be printed. In copper roller engraving the opposite course is pursued, the design being cut out in *intaglio* on the *rounded* surface of the roller, and the impression taken by filling the *incisions* with colour and pressing the cloth into them, both these latter operations being effected by the machine. Further, in the case of block cutting, it is quite impracticable to leave either comparatively fine lines or minute spots in relief, since not only is the utmost skill required to cut them without breaking the grain of the wood, but because, even when successfully cut, they are too weak to withstand the wear and tear of printing. In copper roller engraving, on the contrary, all qualities of line and dot, from the coarsest to the finest possible, may be cut easily, safely, and without the slightest fear of their subsequent damage in printing.

Thus the restrictions imposed upon the treatment of ornament by the nature of block cutting limit the application of block printing to such designs as depend for their beauty upon breadth of effect and boldness of handling.

More delicate results can certainly be obtained by employing blocks upon which the design is built up in strips of metal (a method to be described later), but in no case can a block print, by whatever means it is produced, ever come up to the delicacy of line and stipple possible in roller printing. Appropriate treatment of ornament, therefore, is absolutely essential if the best qualities of block printing are to be brought out.

Another important point to be considered in connection with the limitations of block printing is the question of "repeat." This presents no difficulty at all in cylinder printing, where the pattern can be arranged to fit perfectly on the roller itself; but in block printing, where the cloth is printed by many separate impressions of the block, the pattern must be so arranged that each impression or repeat joins up on every side with the other impressions by which it is

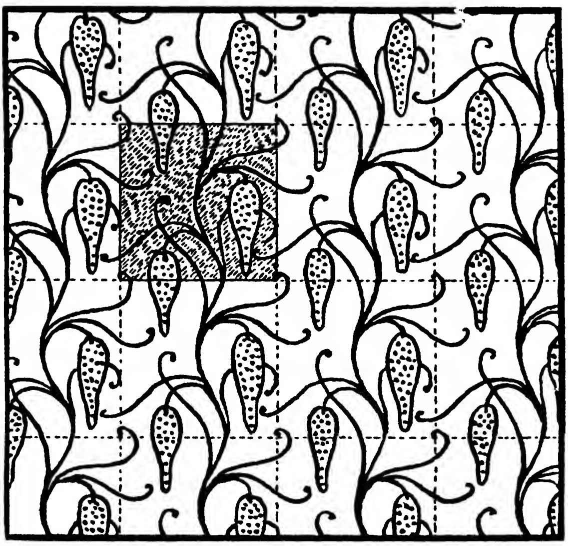


Fig. 1.—Example of a "repeating" pattern.

surrounded. The question of repeat belongs properly to the subject of design; but as it has such an important bearing upon the limitations of block printing, it may not be amiss at this point to give a brief description of what it really is, and to explain how it influences the planning of ornament.

All patterns for calico printing are based upon a regular geometrical figure—square, oblong, diamond, or hexagon—and are so planned that when their opposite edges are brought together, or placed adjacent to each other, all the lines and masses that occur upon them join up exactly and complete the pattern, without leaving any unsightly space or showing any break in continuity of line. This may be achieved in several different ways, which call for no mention here, but the following rough sketches based on the square, and showing the ordinary vertical and side repeats, will sufficiently illustrate the point.

In fig. 2 (representing the darkened portion of fig. 1) that part of the design which falls, within the square ABCD, on the line CD, must appear again or repeat, outside the square, on the line AB; that which falls inside on AC must similarly repeat outside on BD, and *vice versa* in both cases. Every element of the design is thus seen to occur *within the square ABCD*, and to be

arranged in such a manner that when a series of similar squares are placed together with their opposite sides in contact—chess-board fashion—as occurs in block printing, they form a complete pattern (see fig. 1).

To prove whether a pattern will repeat properly or not, it is only necessary to cut it down the centres into four squares (1, 2, 3, and 4, in fig. 2), and then

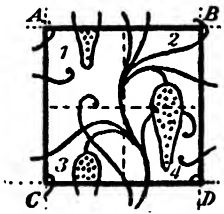


FIG. 2.

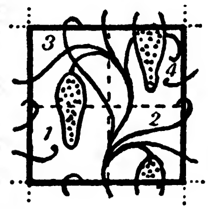


FIG. 3.

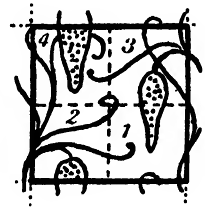


FIG. 4.

(Repeats of fig. 1.)

to transpose them as in figs. 3 and 4, when any defect in the fitting is at once apparent, and can be easily remedied before the pattern is cut on the block.

When a continuous pattern, embodying long unbroken lines or masses of colour, is executed by block printing, these joinings-up at the repeats are always more or less perceptible—a defect due to the necessarily separate application of the block for each fresh portion of cloth printed, and the consequent difficulty of accurately adjusting the successive impressions to each other.

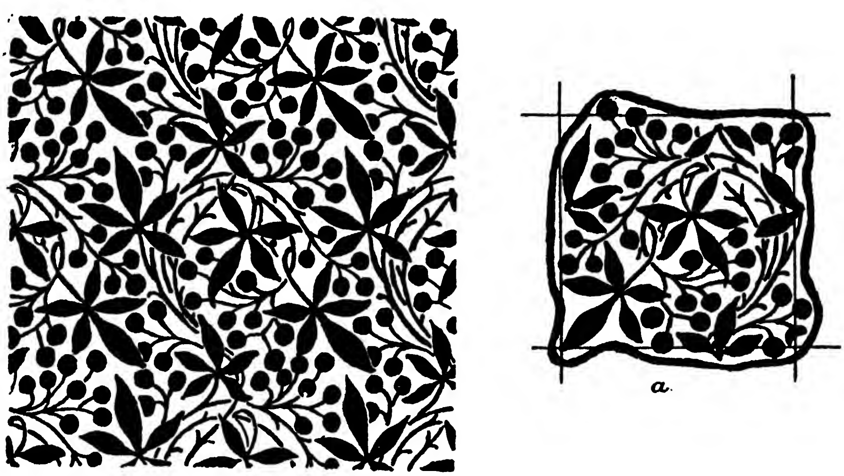


FIG. 5.—A repeating block pattern and sketch (*a*) of the repeat engraved.

They may, however, be rendered practically unnoticeable, in certain styles of pattern, by arranging the repeats so as to occur behind leaves, or at the junctions of stems and branches, etc., or by allowing some of the smaller objects to complete themselves beyond the limits of the square, as in fig. 5, where the design cut on the block appears, as shown at *a*, surrounded by the heavy line (which is, of course, not engraved). A good example of this latter method of working is to be seen at the Manchester School of Technology in a block printed reproduction of a Saracenic pattern executed at the works of, and presented by, the late Sir Thomas Wardle of Leek. To employ an irregularly

shaped block of this kind entails a few extra impressions at each piece-end, but it ensures better work than could possibly be obtained by attempting to print the two halves of a solid object at separate times.

In cylinder or machine printing—a continuous operation—faulty joints at the repeats never occur, being entirely avoided by engraving the required number of side repeats to fit along the length of the roller, and by making the vertical repeats to meet exactly on its circumference. This special facility of roller engraving enables the cylinder machine to be used not merely for patterns that are quite outside the range of block printing, but also for many others which could be executed perfectly by its means.

The nature of block printing precludes any possibility of very fine lines, softened edges, or delicately blended effects of shading over small spaces. A pattern intended for "blocking" should therefore be designed on broad con-

FIG. 6.—Example of graduation in block printing.

ventional lines, with each mass of colour perfectly defined and distinct, and with its detail treated in a suggestive rather than an imitative manner. The number of colours that may be introduced into a block printing design is limited only by considerations of economy in block cutting—a separate block being usually required for each colour. In designs with very long or wide repeats two or more blocks are necessary for each colour, as it is impossible to obtain an uniform impression by hand from a very large block on account of its great weight, which prevents the printer manipulating it properly, and gives rise in consequence to irregular work. Such large-scale patterns are, however, rarely printed, and it is questionable whether the effect obtained is either better than that obtained in the ordinary way, or sufficiently good to justify the increased cost of production. Graduated and shaded effects may also be employed if desired, but as each tint must necessarily be of a distinct shape, easily possible to cut on the block, they are produced, not by the imperceptible merging of one colour into another, as in stipple work on copper rollers, but by placing in juxtaposition a series of suitably shaped patches of colour, which together give the effect of light and shade in a highly suggestive manner. (See fig. 6, a leaf in three shades of olive, copied from a cretonne pattern printed by block.)

When outlines or moderately fine details are designed to occur along with heavy solid masses in the same colour, it is advisable to cut them on a separate block, firstly, because if cut on the same block as the masses, a colour sufficiently thick to print the outlines and details properly would only yield bare and uneven impressions of the masses, which require much thinner colour; and secondly, because, in multicolour patterns, the employment of a separate outline block allows the colourist much greater latitude in arranging and balancing his various colour combinations—a point of no inconsiderable commercial, not to speak of artistic, value.

In cylinder printing, outline and mass are frequently printed from a single roller, good results being ensured by varying the scale and depth of engraving according to the circumstances; but even here the colour possibilities of the pattern are seriously crippled, and in most cases two rollers are engraved, especially if the masses are large and the outlines comparatively light.

Several other minor conditions govern the application of block printing, but from the foregoing brief consideration of its capabilities as compared with those of cylinder printing it will be seen that, irrespective of all other causes, its specific province is marked out, by the nature of the materials and processes employed in its practice, as that of dealing with patterns in which breadth of effect and purity of colour are of more importance than mechanical perfection in the execution of intricate and delicate detail,—in a word, patterns or designs mainly used for decorative purposes.

BLOCK CUTTING.

Formerly wood was used exclusively for the making of calico printing blocks, but as, from time to time, demands arose for more delicate patterns, metal was gradually introduced, for reasons and in ways that will be fully dealt with and explained in the description of each type of block.

I. **Block cutting on Wood.**—For this purpose use may be made of any fairly hard, close-grained wood, such as box, holly, lime, sycamore, plane, or pear. But as box, holly, and lime are only procurable in small planks and are expensive, a block of sycamore, plane, or pear wood is generally preferred in practice.

For large blocks it is customary to combine these woods with still cheaper ones by gluing one thickness of sycamore or other suitable wood to two thicknesses of deal or pine, taking care to see that the grain of each piece runs in a different direction. Before the glue sets, the block is placed under pressure, and is occasionally further strengthened afterwards by screws which pass through each of the three or more thicknesses or layers of which it is composed. The screws are, of course, put in after the pattern is cut, otherwise they would interfere with that operation. Another and better method is to join the several thicknesses together by "tonguing and grooving" in conjunction with glue. Composite blocks made in either of these two ways, while being quite as efficient for printing purposes as those cut out of the solid, possess in addition three great advantages over them, viz.—(1) they are cheaper; (2) they are lighter in weight, and consequently easier to use; and (3) they are much less likely to warp in printing.

The shapes and sizes of blocks for hand printing vary according to the width of the cloth to be printed, the uses to which it is to be ultimately put, and the planning of the design as regards its vertical and side repeats, with which, in cretonne patterns, the lengths and breadths of the blocks are usually made to correspond. If, for instance, cretonne cloth 30″ wide be employed, the side repeats of the pattern must naturally be some divisor of 30″ in order

to allow of some whole number of repeats being fitted into its width exactly —a precaution it is necessary to take for the purpose of avoiding a waste of valuable material when two widths of it are required to be joined or sewn together without exhibiting any interruption in the "run" of the pattern. The blocks for such a cloth would therefore have a width of 5", 6", 7½", 10", or 15", which would permit of six, five, four, three, or two whole side repeats being fitted exactly into the 30 inches of width. The vertical repeat of a pattern is quite independent of the width of its side repeat, and may be any convenient length desired; but it must be remembered that the larger the block, the more difficult is it for the printer to adjust the various impressions accurately, and therefore the more uncertain are the results of printing. For this reason block printing patterns rarely exceed 20 inches in vertical repeat, as otherwise the block would be too heavy for the printer to handle with any degree of comfort, speed, or precision. A usual size for cretonne patterns is 15" × 15"; sometimes 20" × 15" is used; but if the design is on a larger scale, say 30" × 15", or 30" × 30", two sets of blocks, each carrying half a repeat, are usually necessary to ensure the best results.

As a general rule, blocks are either square or oblong, but sometimes they are diamond-shaped, and frequently take an irregular form, as shown at fig. 5, *a*. In any case, of whatever size and shape, and whether simple or composite, wood blocks for textile printing must always be between 2½" and 3½" thick, for the reason that the thicker they are, the less liable are they to warp, crack, or get twisted out of shape by the prolonged contact with wet colour to which they are subjected during the printing operation.

Although block cutting, generally speaking, is only a refinement of the primitive art of carving in flat relief, its successful accomplishment for the purposes of textile printing (especially if the design be at all intricate) calls for the utmost care and attention on the part of the worker, and demands of him a sureness of eye and delicacy of hand that can only be attained by long practice and experience of the craft. Being one of the many distinct trades of which calico printing is made up, its full discussion here from a technical point of view would occupy too much space; but as some knowledge of the various practical methods of reproducing a design is essential to a proper understanding of their respective scopes, the following short description of the actual process of block cutting will perhaps help to make clearer what has already been said respecting the particular possibilities of hand printing from wood blocks.

A suitable piece of wood of fine, even grain, and free from all defects, such as knots, cracks, etc., having been chosen and cut to size, its working surface is first of all planed up to a dead level, and then, if necessary, further smoothed with fine sandpaper. Upon the perfect flatness of this surface depends entirely the evenness of the resulting print; for no amount of skill in printing can remedy the irregularities caused by low places on the face of the block. The next step in the process is the transference or "putting on," as it is termed, of the pattern. For this purpose a careful outline tracing of the design, made with a mixture of lampblack and linseed oil, on transparent tracing-paper, is laid face downwards upon the smooth, level surface of the block, and transferred thereto by rubbing it gently from the back with either the thumb-nail or an ivory burnisher. The "putting on" completed, those portions of the design to be preserved in relief are tinted with some water-resisting colour—an ammoniacal solution of cochineal is generally used, and is as good as anything—after which the block is given into the hands of the cutter, whose work consists in removing the ground between the coloured parts. He commences by thoroughly damping the block (in which condition it must be kept until finished by being wrapped in damp cloths during the night), and

then proceeds to cut away the untinted parts of the wood round about the larger objects, leaving the more delicate work until the last. The depth to which the ground is sunk varies considerably. For large objects it may be any depth from $\frac{1}{4}''$ to $\frac{3}{4}''$, but it decreases in proportion as the objects become smaller or are massed closer together, as, for instance, in the case of the petals of a small flower. Usually, too, the sides of the outstanding parts of the block, instead of being cut vertically downwards, slope outwards a little, in order to retain as much of the strength and original solidity of the block as possible.

The tools used in wood block cutting are practically the same as those used in ordinary fine carving. They include various sizes and shapes of chisels, gouges, and drills, together with instruments something like surgical scalpels or penknife blades, which are employed chiefly for trimming up edges and cutting straight lines. When the whole of the uncoloured portions of the block have been cut out to the required depth, the pattern stands up in relief in the same way as letterpress type, only more so. It only remains now to verify the accuracy of the repeats by a practical trial and add the "pitch pins." These latter are small pins of brass driven in, at the corners of the block, down to the level of the printing surface, and so adjusted as to position that in printing, when those on the right-hand side of the block are placed over those on the left-hand side of the previous impression, the repeats of the pattern correspond exactly. Sometimes, to prevent the block from absorbing an unnecessary amount of moisture from the printing colour, the cut-out portions are varnished; but when this is done great care must be taken not to drop any varnish on the printing surface, as any difference in texture is apt to give rise to unevenness of colour in the resulting work.

It frequently happens in printing large, solid masses from wood blocks that either the edges are clumsy or that the colour is unevenly distributed. The first successful attempt to overcome these serious disadvantages was made by forming the outlines of such solid masses from strips of copper or brass hammered into the face of the block deeply enough to hold them securely in place, and at the same time leave them projecting sufficiently far for the purposes of printing ; the spaces between the outlines thus formed were then filled in with felt, which, being more porous than wood, absorbed more colour, and consequently gave a fuller impression. The clumsiness of the edges was prevented by the narrow fillet of metal, which only took up a little colour—just sufficient to print the cloth, without spreading beyond its proper limits when the block was struck with the mallet of the printer. Later on, this process was replaced in many instances by the simpler and cheaper method of "flocking." In flocking, the face of the block is first varnished and then dusted with finely divided woollen flocks or "fluff" ; after thoroughly drying, the varnish is applied a second time by dabbing, and the block placed face downwards on paper covered with the same fluff, and left there until the varnish is perfectly dry and hard. It is then removed, the excess of fluff is dusted off, and after the edges of the design have been trimmed up with a sharp knife the block is ready for use. Both the felting and flocking of blocks are still in general use, but the former appears to be most favoured in England.

The number of blocks required to realise any ordinary design must correspond to the number of colours employed in that design. As each block, therefore, only represents one colour, separate tracings must be made of the portions of the design occupied by each colour, and transferred by the "putter-on" to separate blocks, which are then cut and treated as already described. Thus for a design containing red, pink, yellow, two greens, blue, and an outline, seven separate blocks would be required, and the cloth would require printing seven times—once for each colour. It is this which makes block-printed goods

Fig. 7.—Dark olive.

Fig. 8.—Medium olive.

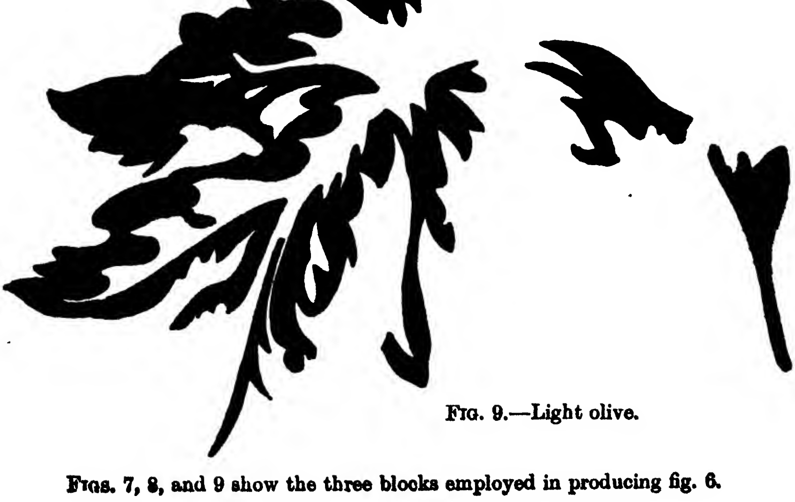


Fig. 9.—Light olive.

Figs. 7, 8, and 9 show the three blocks employed in producing fig. 6.

so expensive when compared with those printed by machine from copper rollers —a method in which all the colours are printed at a single operation, and at a speed some hundreds of times greater than that of hand block printing.

Some idea of the curious appearance presented by the separate colour blocks of a multicolour pattern may be obtained by referring to the three rough sketches on page 25 (figs. 7, 8, and 9), which represent those portions of the three olive blocks used to produce the complete leaf shown in fig. 6.

Such, in brief, is the outline of wood block cutting, a method eminently adapted to yield rich, broad, decorative effects, but, as previously pointed out, quite inapplicable to designs embodying fine outline and delicate detail. When patterns of this latter class are intended to be reproduced by block printing, recourse is had to the following method of "coppering."

II. **Coppered Blocks.**—In the process of "coppering," the design, instead of being cut out of the solid wood, is built up on the flat surface of the block in strips and rods or pins of copper or brass. By this means spots and lines, varying in width from $\frac{1}{64}''$ to $\frac{1}{16}''$, can be obtained easily, and of ample strength to withstand the shocks of printing. Moreover, many delicate little forms, which are either impracticable or too fine to cut on an ordinary wood block —such as ovals, rings, diamonds, stars, rosettes, etc.—are easily capable of realisation on a coppered block by simply inserting short pieces of rod or tubing corresponding in section to the shapes desired. For making these small objects, brass rod or tubing is drawn, in long lengths, through a steel drawplate perforated with holes of the required shape; short pieces of the necessary length are then cut off, and when a number of these are driven into the face of the block they furnish a series of objects identical in shape, size, and height. For solid objects brass rod is used; for those in outline brass tubing.

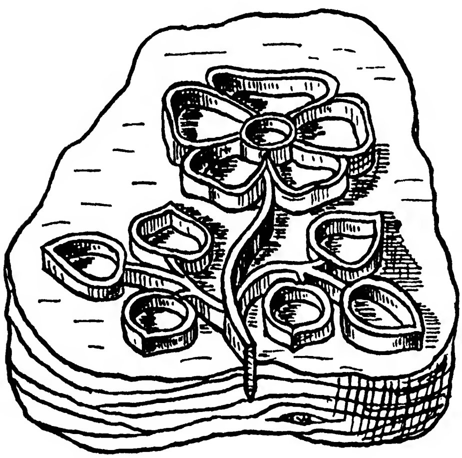


FIG. 10.—Portion of a "coppered" block.

In the making of a coppered block the pattern is transferred or put on in the usual way, but the cutter, instead of removing the ground, as for wood blocks, only works on the outline, which he cuts out with suitable tools to a depth of about a quarter of an inch. The holes for the insertion of the pins, etc., for spots, etc., are drilled out at the same time. The pins and strips (or ribbons) of brass are then hammered edgewise into the cut-out lines until the necessary projection is attained—about $\frac{1}{8}''$ above the level of the block; the face of the block is then filed or ground on a flat stone table until every piece of brass stands at exactly the same height, after which any distortion of the lines or displacement of the smaller objects caused by the filing, grinding, or hammering is corrected with pliers of convenient shape. Finally, the whole working surface of the block is polished with fine emery-paper, and after the pitch pins are adjusted the block is ready for use. Fig. 10 shows a portion of a coppered block.

Coppered blocks, besides being capable of rendering much more delicate effects than are possible to obtain from wood blocks, possess three further

advantages over them, viz.—(1) their working parts being entirely of metal, they neither swell nor warp out of shape under the action of wet colour; (2) they are more easily repaired, and consequently are more serviceable; and (3) the brass strips and pins of which the pattern is composed being of the same width throughout their substance, it is only necessary, when the block becomes uneven in surface from constant use, to file it level again, when it will give precisely the same impression as at first. This levelling-up cannot be done on wood blocks because, as a rule, the parts in relief increase in width as they recede from the surface (especially so in the case of lines and small objects); so that if it does become needful to level-up a wood block, the whole of its pattern will require to be re-cut at the edges to bring each object back to its original dimensions.

On the other hand, coppered blocks yield a more mechanical and harder effect than those of wood, mainly on account of the fact that the outline they give is of uniform thickness throughout its entire length. In the older process of wood cutting the quality of line can be varied at will (so long as it is kept thick enough), with the result that it offers to the designer greater opportunities of giving expression to his work. Coppered blocks, too, unless, of course, felted as well, are quite unsuited to the printing of heavy, solid masses of colour, and therefore they are only used for fine outlines and delicate touches, like the veining of leaves and similar light work.

III. **Cast-metal Blocks.**—In addition to the two methods of block making already described, a third is frequently employed for small patterns (and those made up of many similar detached objects), where it is necessary, on both technical and economical grounds, to put several repeats on the same block. In these cases a great reduction in the time and cost of making blocks has been effected by the introduction of stereotyping—a method whereby as many castings of the repeat of the pattern as may be required are made from one mould, and afterwards arranged to fit, and screwed securely in place on a plain block.

The first attempt in this direction was made by casting type-metal in plaster of Paris moulds or matrices taken from patterns cut on ordinary wood blocks; but it was soon abandoned on account of the expense incurred by having, almost invariably, to make a new mould for each casting required. This necessity arose from several causes : in the first place, the high relief of blocks for calico printing made it exceedingly difficult to completely fill all the interstices of the pattern with the plaster; secondly, it was almost impossible to separate the mould from the model without damaging the finer parts; thirdly, during the drying and heating of the moulds they were very liable to crack; and fourthly, when a casting was withdrawn from a satisfactory mould, it usually happened that the more delicate portions of the mould broke off and stuck in the corresponding parts of the casting. In addition to all these risks, the time occupied in trimming up defective castings, and the cost of plaster and of fuel for drying, were also heavy items in the cost of production. After many unsuccessful trials to overcome these various defects in plaster moulds, an ingenious means was eventually devised of making a modified wood block itself serve as a mould. The method of working is as follows:—

On a perfectly dry and well-seasoned block of lime or pear wood, sawn across the grain (so that the latter runs at right angles to the working surface), and rather larger in area than the casting required, the outline of the design, or rather one repeat of it, is built up in brass, just as in the coppered blocks described above. The strips may vary in thickness in different parts of the pattern according to the kind of line required, but each separate strip must be of uniform thickness, and all must be of exactly the same breadth. The design

is now put on the block and the strips driven in to the predetermined depth, leaving at least ⅛" projecting above the surface of the wood. It need hardly be said that every strip of brass must penetrate the wood to exactly the same depth. The pattern completed in this way is then surrounded with a brass border screwed round the outside of the block, and slightly higher than the pattern itself. All the metal parts are then well cleaned and painted with zinc chloride, after which the block is placed face downwards in an iron tray containing a flat cake of previously melted and cooled solder, corresponding in thickness to the amount of the projection of the brass pattern on the block. Heat is now applied under the iron tray, and the solder, in melting and alloying itself with the *outstanding* portions of the brass, transmits at the same time sufficient heat to the *inserted* portions to carbonise the wood immediately in contact with them. On cooling, and taking out the border screws, the brass is found to be firmly embedded in the solder, and the two together can be readily detached from the block by a gentle tap on the back with a hammer, thus leaving a mould of the original pattern burnt in the wood. The mould is now well dusted with chalk or blacklead, and, after blowing away the excess of powder, is provided either with a cardboard or brass border about ⅛" high, which converts it into a shallow tray, with the pattern on the bottom burnt out in intaglio. The casting is effected by pouring in molten type-metal up to the level of the top of the border, taking care at the same time to tap the mould smartly once or twice before the metal commences to set, for the purpose of causing it to flow into and completely fill every part of the pattern. When cool, the casting is taken from the mould, and its edges, and such other parts as require it, sharpened up by filing or scraping. A sufficient number of repeats of a pattern made in this way are adjusted on a plain block of wood so that they join or fit to each other exactly, and are then permanently secured to it by means of screws or nails. Finally, the block is laid face downwards on a stone or iron slab and ground with emery or sand until all the castings are of exactly the same level.

When it is intended to print solid masses from this kind of block their outlines only are cast, the spaces between them being filled in with felt. If cast solid they would take colour very badly, and give a clumsy and uneven impression.

A simpler, cheaper, and more expeditious method of making wooden moulds was invented by Burch of Accrington, whose patent typing machine burns out the pattern directly, and thus dispenses with the necessity of inserting strips of brass, etc. The machine consists essentially of small steel punches, of various shapes and gauges, heated to the requisite temperature by the flame of a small gas blowpipe or a bunsen burner, and capable of being raised or lowered to any desired extent by means of a lever actuated by the foot of the worker. The whole is mounted in a framework similar to that of the ordinary drilling machine used by engineers—a machine which it resembles very closely, the only radical difference being that the punches do *not* revolve. To make the matrix or mould, the block, with the pattern previously drawn upon its surface, is first placed under the heated punch ; this is then lowered and burns its way through the wood to the proper depth, the lines of the pattern being followed by steadily moving the block about by hand whilst in contact with the punch. When one part of the design is completed the punch is raised, and another part of the block then brought under it, ready to undergo the same operations, which are repeated until the whole mould is finished.

In a later development on these lines the heated steel punches are replaced by revolving drills; in all other respects the procedure of mould-making is the same.

THE OPERATIONS OF PRINTING BY HAND.

In addition to engraved blocks, two other pieces of apparatus are required for the printing of calico by hand, viz. the sieve which supplies colour to the block, and the printing table upon which the cloth to be printed is extended.

The sieve (fig. 11) is composed of three separate parts: (1) the sieve proper (*a*), consisting of a wooden drum, covered at one end with a head of fine woollen cloth stretched over it tightly and secured by nails; (2) a similar but rather larger drum (*b*), covered with waxed cloth or thin mackintosh; and (3) a tub (*c*), almost filled with old colour or flour paste—commonly known as the "swimming-tub"—and of sufficient size to allow of the second drum (*b*) floating freely on the surface of its contents without much lateral play. The object of the swimming-tub is to provide the elastic support necessary to enable the colour-charged woollen sieve (*a*), when placed upon it, to give up its colour evenly and regularly to the block. A separate woollen sieve is required for

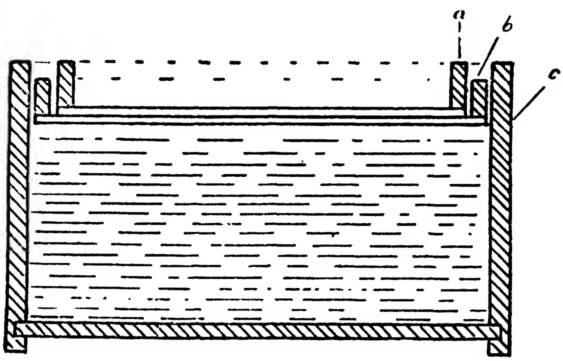


FIG. 11.—Sieve and swimming-tub.

each colour, but the same swimming-tub may be used over and over again for as many sieves as will fit it. The sieves are not necessarily round, but may be either square or oblong if more convenient for working.

The printing table (fig. 12) is made of perfectly flat slabs of stone, iron, or concrete (*a*) 2″ to 4″ thick, covered with a printer's tightly stretched woollen blanket (*b*), and supported on a strong and rigid framework of wood. Its dimensions vary considerably according to the cloth to be printed, but a usual size is 8 ft. long, 3 ft. broad, and 3 ft. high.

At one end the framework is provided with brackets (*c*) for carrying the rollers (*d*, *d*), on which are wound respectively the "sets" of the cloth for printing and of the "back grey"—a piece of unbleached calico used for protecting the blanket from the colour which penetrates through the white cloth during the printing. At the other end of the framework another bracket supports the roller (turned by hand) used for drawing forward the back grey.

Beyond and above the printing table a series of hanging rollers are suspended from the roof of an upper storey for drying purposes. Formerly the printed pieces were simply allowed to hang in loops from these rollers until sufficiently dry to be taken down, but at the present time many tables are furnished with steam-heated drying chests (*f*, *f*, *f*), situated between a double series of rollers (*e*, *e*, *e*), over which the cloth is drawn by hand. Any distortion of the partly printed pattern, due to the stretching of the cloth under excessive

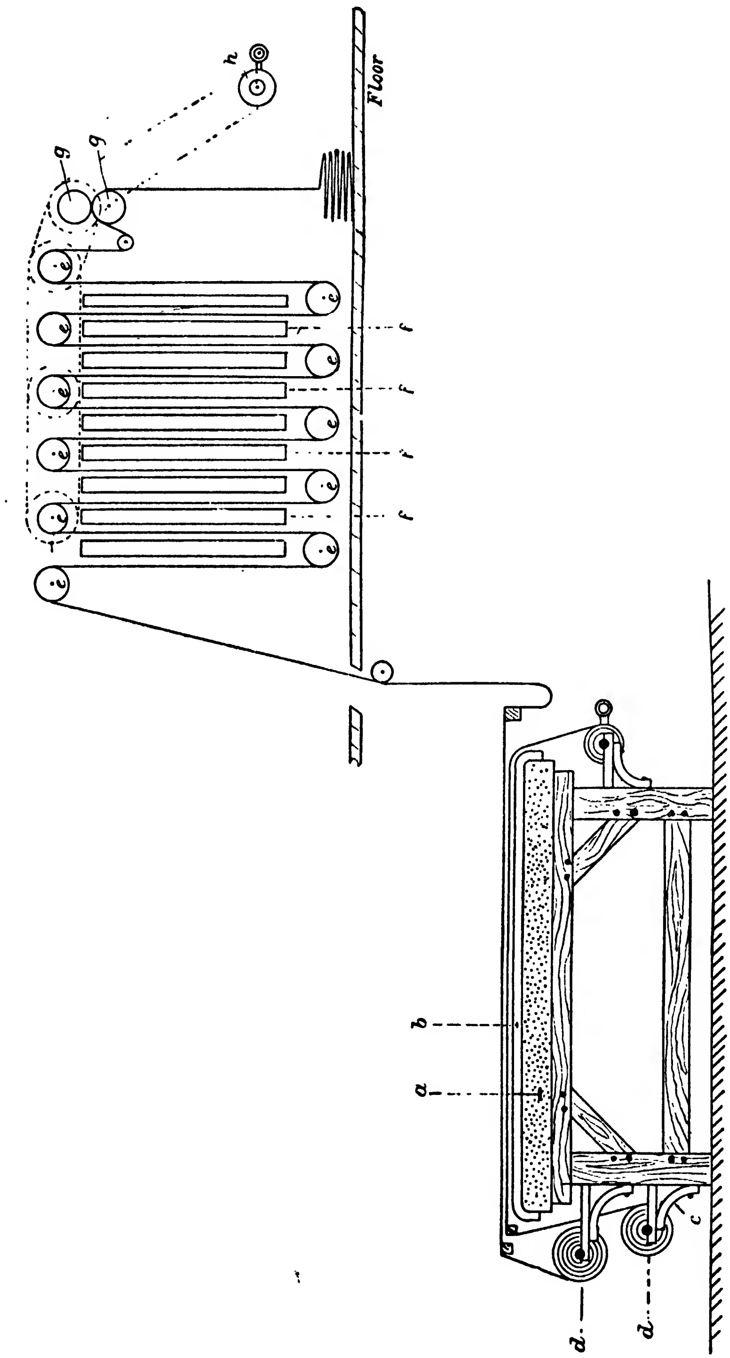


FIG. 12.—Printing-table and accessories.

tension, is avoided by gearing several of the upper rollers with the draw rollers (*g*), and driving by means of a strap connecting the latter with the hand wheel (*h*) below.

The actual printing is performed as follows:—The woollen sieve, previously saturated with the suitably thickened colouring matter, is placed on the waxed cloth head of the drum (*b*) of the swimming-tub, and is then again coated with colour, spread over it evenly with a flat brush by a boy called the "tearer." The printer now charges the face of the block evenly with colour by pressing it twice, in different directions each time, on the sieve, and then applies it to the cloth stretched on the table, ensuring a full impression of the pattern by striking the back of the block with a heavy wooden mallet. It is important that the first row of impressions across the width of the cloth should be exactly at right angles to the selvedges, otherwise the pattern, if properly fitted at the repeats, would gradually run off the edges of the cloth at one side, and tend to approach the centre at the other; in short, it would be crooked, and would require extra impressions to fill the cloth. The printer therefore rules guiding lines on the cloth for the first and sometimes also for the second row of repeats, and thus avoids any mistakes he might make if he trusted to his eye alone. The first impression printed, the tearer re-charges the sieve with colour, and the printer proceeds with the second and succeeding impressions in precisely the same manner, taking care to make each join up or repeat properly by placing the pitch pins at the top and on one side of the block, exactly over those already printed, by the bottom and the opposite side at the previous impressions. When the two or three yards of cloth lying on the printing table have been printed, they are drawn over the hanging or drying rollers, and at the same time an equal length of fresh cloth is unwound from the roller at the end of the table and drawn forward over it, ready to undergo the same operations, which are repeated again and again until the whole of the cloth on roller is fully printed.

In multicolour patterns containing superpositions—that is, the falling of two colours together to form a third—or where each colour in some part fits up closely to all the rest, it is usual, in order to prevent them spreading into each other whilst wet, first to print the cloth throughout with one block; then to dry it, re-wind it on the set, and print it with the second block, fitting or registering the second colour accurately in place by means of the pitch pins, with which every separate block of a pattern is furnished, and without which it would be almost impossible to obtain correct registration. The third colour is applied in the same way, the process being repeated as many times as there are colours in the pattern. Where, however, the various colours are distinctly separated from each other, as, for instance, in patterns made up of differently coloured spots or other detached patches of colour, they may, if desired, be printed immediately one after the other without removing the cloth from the table.

For the purpose of facilitating the correct registration of the repeats of a pattern, the cloth used in block printing is sometimes stiffened a little to prevent it from wrinkling during the progress of the work. As a rule, a single run through a three-bowl calender is sufficient for this purpose, but very soft, lightly-woven goods often require to be further assisted by a run through a thin solution of gum or starch paste, followed, after drying, by calendering.

The majority of patterns, as already pointed out, require as many blocks for their reproduction as they contain colours, but in certain classes of design, where the colour-masses are entirely separate or stand clear of each other, it is possible, by modifying the construction of the sieves and the method of supplying them with colour, to print several colours at once from *one* block.

thereby effecting a considerable saving in time, labour, and the cost of block-cutting.

"Toby" Printing.—Whenever, for example, the several colour-masses of a design are entirely detached from each other, and lie, moreover, at some little distance apart, they may be all cut on one block and printed at one operation from a divided or "tobying" sieve of the following ingenious construction:—Over a wooden block, hollowed out into shallow compartments (*a*, *a*, *a*, fig. 13, plan), varying in size, shape, and number according to the requirements of the design, a fine woollen sieve cloth (*d*, fig. 13, section) is stretched and cemented with a mixture of pitch and resin to the tops of the dividing walls of the compartments; a thick string *e*, *e*, *e*, *e*, well soaked in the same pitch-resin mixture, is then cemented *over* the cloth, along the outlines of the compartments, and

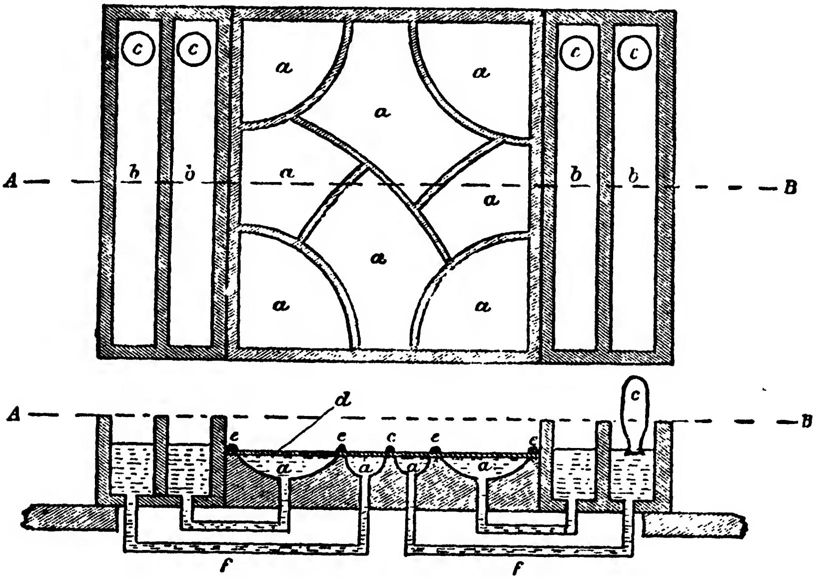


FIG. 13.—Tobying sieve.

by forming little ridges on the surface of the sieve, prevents the different colours from intermingling at their edges.

The compartments are supplied with colour from below through the connecting-tubes *f*, *f*, *f*, *f*, which communicate with the colour boxes *b*, *b*, *b*, *b*, arranged at the sides of the sieve. With a sieve constructed as shown in fig. 13, it is evident that eight distinct colours could be printed from one block, but, for the sake of simplicity, only four colour boxes are shown. These colour boxes are filled to a height a little above that of the sieve itself, so as to exert a gentle pressure on its under side and help the colours to force their way to the surface. A constant level is maintained in practice by the simple expedient of filling the bottles *c*, *c*, *c*, *c* with colour, inverting them in the boxes, and finally adjusting them so that their mouths rest upon the surface of the colour at exactly the right height above the sieves. Their mode of action is obvious.

Printing from a toby sieve is performed as usual, except that, in order to ensure the correct colouring of every impression, the block must always be applied to the sieve in the same way; not dipped in two different directions, as required for ordinary block printing. To enable the printer to do this with

certainty every time, and thus furnish every part of the pattern with its proper colour, the block is provided with projecting gauges, which fit into corresponding notches on the sides of the sieve, and will fit nowhere else.

The consistency of the colour used in tobying exercises considerable influence on the result. If it is too thick it will not pass through the sieve; if too thin, it "floods" the sieve and gives a clumsy impression. Natural gums of the gum Senegal class are usually preferred for thickening purposes, on account of the fact that in even comparatively thin solutions they still retain sufficient body to print well.

Rainbowing (Fr. *fondu*).—Another method of obtaining multicoloured effects from one block is known as "rainbowing," and is adopted when the colours are intended to melt gradually into one another. It differs only from

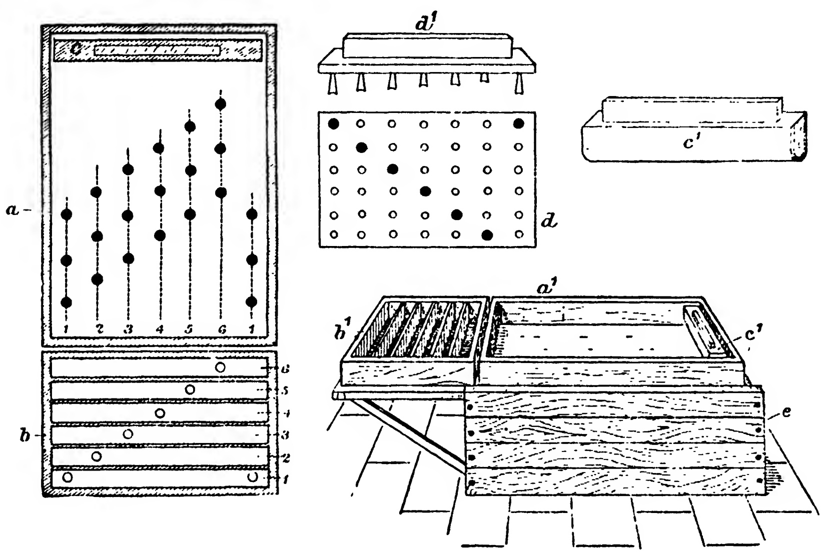


FIG. 14.—Rainbowing or "fondu" apparatus.
a, a', the sieve; *b, b'*, the divided colour box; *c, c'*, the spreader, covered with cloth; *d, d'*, the colour lifter; *e*, the swimming-tub.

ordinary block printing in the means employed for furnishing the sieve with colour. This is done by a special *colour lifter* that deposits the various colours in little pools across the width of the sieve, over which they are then spread lengthwise in the form of overlapping stripes with a spreader—a wooden roller or a half-round piece of wood. The colour lifter consists of a board of wood of the same area as the colour box, provided on one side with a handle and on the other with a series of adjustable pegs or brushes, so arranged that when they are dipped into a divided colour box each peg falls into a certain compartment and takes up its own particular colour. The sieve and swimming-tub are of the usual construction, but rectangular in shape; for convenience of working the latter is fitted at one end with a shelf, upon which the divided colour box is placed so as to be in close proximity to the sieve. As in tobying, the block works against gauges to ensure that it is always dipped in the same place on the sieve. Fig. 14 will give some idea of the apparatus for rainbowing as it appears in plan and perspective.

If it be required to produce, say, a side-repeating spectrum or rainbow

effect in six colours, the divisions of the colour box may be filled as follows:—In No. 1 is put red; in (2) orange; in (3) yellow; in (4) green; in (5) blue; and in (6) violet. The lifter, with its pegs placed in the holes indicated by the black dots in *d*, fig. 14, is then dipped two or three times in the colour box, and transferred quickly, after each dip, to the sieve, when the adhering colour drains off the pegs and is deposited on the sieve in the positions shown by the black spots at *a*, fig. 14. When a sufficient number of pools of the various colours have been transferred in this way, they are joined up into stripes with intermingling edges, and distributed over the entire length of the sieve, by moving the spreader backwards and forwards from end to end of *a*. The printing is done as usual, except that if the block is applied more than once to the sieve it must, of course, always fall on the same stripes, otherwise the effect would be spoiled.

By altering the position and number of the pegs in the lifter and changing the colours in the box, it is obvious that many rich and beautiful shaded effects can be obtained readily by rainbowing; such, for instance, as printing each block of a multicolour pattern in gradated tints of its own particular colour, on either a flat or shaded ground; or producing from a plain block various stripes, differing in shade and distance apart according to the disposition of the colours on the sieve.

Notwithstanding that rainbowing is capable of yielding striking effects, it is very rarely used at the present time, much more regular results being obtained by machine, and at a tithe of the cost. Toby printing, on the other hand, is still employed for filling in the brightly coloured parts of certain styles of handkerchiefs, the grounds of which have been dyed; but it, too, has lost most of its former importance, and is now only used in conjunction with roller printing for a very small proportion of some of the coarser export work.

Many other additions to, and modifications of, the apparatus described in connection with the above methods of block printing have been suggested from time to time, and even made use of; but as they are quite obsolete and have no bearing on modern practice, they call for no special mention in a work of this sort.

(2) BLOCK PRINTING BY MACHINE.

It will be evident from the foregoing descriptions that the labour of hand printing from small blocks must be enormous, and that no high rate of output is possible. This latter disadvantage was recognised in the early days of calico printing, when, to supply the demand for a popular pattern, it frequently became necessary to cut three or four sets of blocks for it, and print them simultaneously by as many printers. The great expense thus incurred naturally set the problem of printing from large blocks by machinery, and finally led to the invention of the "surface" printing machine, and later the "perrotine."

The pioneers in this direction displayed a vast amount of ingenuity in trying to adapt the principle of the typographic machine to the conditions of calico printing; but of all the numerous attempts made on these lines only two achieved any degree of success, viz. the machines of Watt in England and of Depouilly in France.

As both machines are now of historical interest only, no further mention of them need be made beyond saying that they were only capable of printing one colour at a time, that they were only suited to coarse work, and that they foreshadowed most of the principles afterwards so ingeniously applied in the perrotine—a three-colour block printing machine, invented in 1834 by Perrot of Rouen, who, ten years later, further improved it to print four colours.

(*a*) **Perrotine Printing.**—Besides printing three or four colours at once, the perrotine also performs mechanically all the other operations connected with the actual process of printing, viz. the charging of the sieves with colour; the transferring of the colour from the sieves to the blocks; the stamping of the blocks on the cloth; and the moving forward of the cloth, after each impression, a distance equal to the width of the block, so that a fresh portion of the cloth is brought into such a position that when the next impression is made its repeats join up exactly with those of the previous one.

As compared with hand printing, the perrotine possesses the advantages of (1) printing the whole width of the cloth at one operation; (2) of giving an enormously increased rate of production—250 per cent., according to Persoz; (3) of yielding a superior quality of work as regards the accuracy of the fitting of the repeats and the registration of the different colours; and (4) of making it possible to print comparatively fine line patterns—such as open-line checks—with a certain degree of precision. On the other hand, the employment of the perrotine is restricted to patterns not exceeding 5½″ in vertical repeat, and not containing more than three colours, or at most four, though it is questionable whether the four-colour machine was ever used to any extent. Such effects, too, as are obtained from the toby sieve are quite beyond the capabilities of the perrotine; but rainbows or *fondus* may be produced in several additional colours by suitably dividing the colour boxes which supply the sieves.

In designing for the perrotine, superposition of colour is also best avoided as much as possible, because in block printing, where the colour lies more or less on the surface of the cloth, if two wet colours fall together on the same spot they invariably spread out beyond their proper limits and result in a clumsy impression.

The blocks used in the perrotine machine are made in one or other of the ways already described, and are usually 30″ long by 3″ to 5½″ broad, according to the pattern and size of the machine. The machine itself is exceedingly complex in its construction and working, but the following description and the diagrammatic sketch will give some idea of its mode of action. It consists essentially of five separate parts, viz.—(1) the printing tables, which are stationary; (2) the sieves; (3) the mechanical tearers, comprising a brush and colour boxes; (4) the block carriers, which are actuated by delicate machinery in such a way as to impart to them a motion very similar to that produced by the human hand when it presses the block on the cloth during the printing; and (5) an ingenious arrangement for drawing the cloth forward after each impression.

The tables *a*, *a*, *a* are of cast iron, 36″ long and 6¼″ broad, and are arranged, as in fig. 15, at right angles to each other, forming, in a sense, the three sides of an incomplete four-sided prism. At each corner of the square thus formed is situated a guide-roller, covered with pins to prevent the cloth from slipping, and around these four rollers R, R, R, R and the three tables the cloth to be printed, together with a blanket and a back grey, circulates in a regular, though intermittent, way. The sieves *e*, *e*, *e* consist of a framework, over which is stretched a piece of stout woollen cloth free from nap, and each sieve is provided with a to-and-fro motion, which allows it to move away from between the block and the table as soon as the former has received its charge of colour. The colour boxes *c*, *c*, *c* are furnished with rollers—one partly immersed in the colour and the other above it, but in contact with it, and regulated so as to work against the sieve when it moves away from the block. The brushes *d*, *d*, *d* are for the purpose of distributing the colour over the sieve in a smooth, even coating; they may be either stationary or given a slight reciprocating motion for the better equalisation of the colour charge. The block carriers *b*, *b*, *b* are of cast

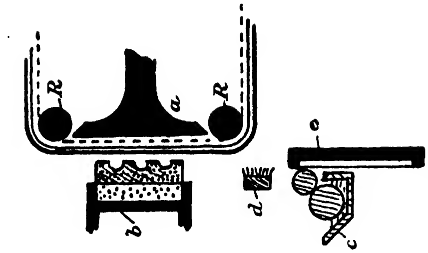


FIG. 16.

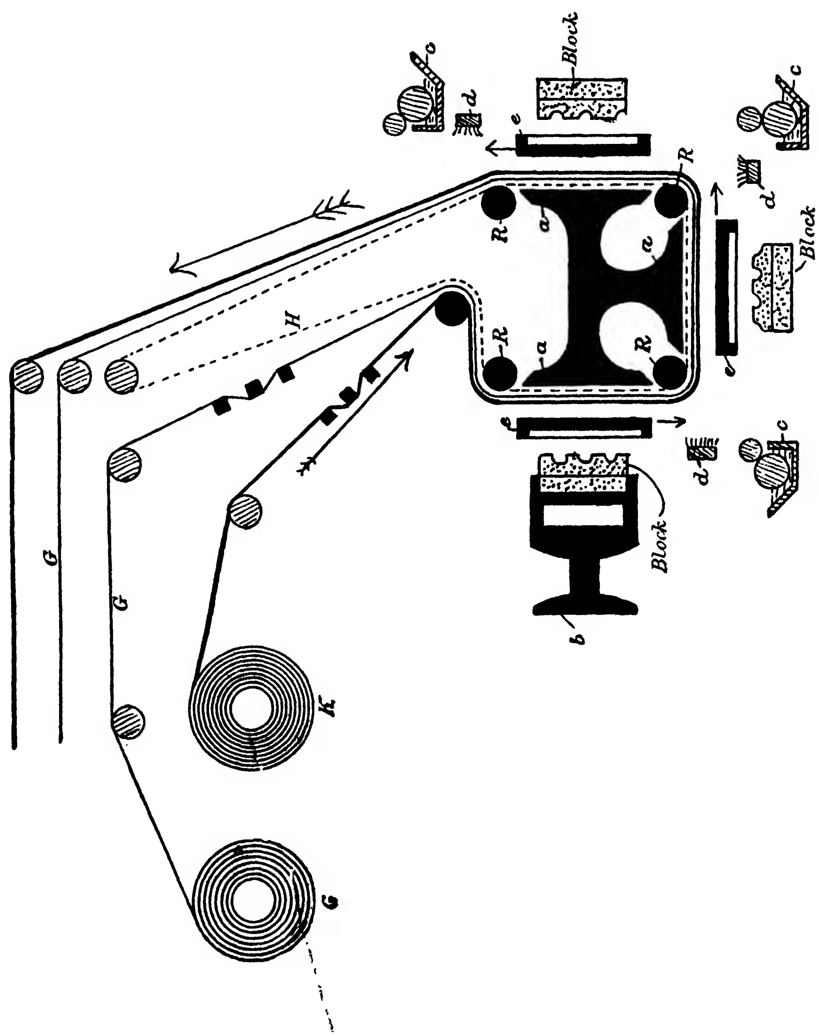


FIG. 15. Diagrammatic sections of the "Perrotine."

iron, mounted in slides or guides which ensure their perfect parallelism of motion—a necessary condition if perfect fit and evenness of impression are to be obtained.

The working of the perrotine is somewhat as follows:—

The first block and its sieve being in the position shown in fig. 16, the first effect of setting the machine in motion is to cause the sieve to move upwards against the colour-furnishing roller in the box *c* and the brush *d* until it reaches the position shown in fig. 15. At this point the block is pushed forward and gently pressed against the colour-charged sieve, thereby receiving its own charge of colour; this is repeated, and then the sieve moves back again to its original position (fig. 16). Whilst the latter movement is in progress the cloth from the roll K, the back grey G, and the blanket H all advance on to the table, and immediately the sieve is quite clear of them the block advances and stamps the first impression on the cloth. The block now recedes, the sieve rises once again to the position in fig. 15, and the same cycle of operations is repeated on a fresh portion of the cloth, which has moved forward towards the second table after the first impression. The second impression of the *first* block being completed, the *second* block and its accessories are put into motion, with the result that as the third impression of the first block is made, its first impression comes on to the second table and receives the second colour of the design from the corresponding block. In exactly the same way the cloth passes under, and is printed by, the third block, so that as it emerges from the machine it is fully printed in three colours, and with a perfection and at a speed quite beyond the powers of a hand block printer.

It ought to be mentioned that each block may be worked independently of the others, and consequently, by stopping two blocks and the cloth, the third can be made to print twice on the same part of the cloth if it be thought that the first impression was too weak.

Continental calico printers were not slow to recognise the advantages offered by the perrotine, and, in spite of its obvious limitations, it rapidly superseded to a considerable extent the hand printing of three-colour block patterns. For some reason or other it never found much favour with English printers—possibly because they may have thought that the days of block printing were numbered, and, in consequence, have devoted all their energies to the development of the roller machine. In France and Italy, however, it is still in use, and at the present time many fine prints are produced either wholly or in part by its agency.

(*b*) **Surface Printing.**—Another and totally different system of block printing by machine—earlier in date than the perrotine, but less important for textiles—is known in England as " surface printing " or " peg printing."

It is of French origin, and was invented by Ebinger in 1800 (thirty-four years before the perrotine) for the purpose of imitating, as nearly as possible, English work printed on the cylinder machine from engraved copper rollers—a process unknown in France at that date. Ebinger was so far successful in his aim as to hit upon the correct principle of continuous printing, viz. by passing the cloth between a cylinder covered with a woollen blanket, which acted as the printing table, and an engraved roller furnished with colour from a plain one working in a colour box below; but in other respects his machine was of the most primitive description, and utterly failed to achieve the object of its invention. It was tried at both the Jouy and Beauvais printworks, but was eventually abandoned for the following reasons:—(1) the rollers being entirely of wood, rapidly got warped by the action of the wet colour and became quite useless, thus entailing considerable expense in block cutting; (2) the system

of supplying the block with colour was defective, and resulted in uneven work; and (3) the impression made was inferior to that obtained from an ordinary flat block.

Some years later Burch, of Peel's Works, at Church, Lancashire, made experiments in surface or continuous relief printing; and after studying the causes of Ebinger's failure, finally succeeded in establishing the conditions essential to its practical application. The first defect of Ebinger's machine—warping—he overcame by applying to his pattern rollers the method of coppering and felting already described. The wooden foundations of the pattern rollers were further protected from dampness by a thick coating of waterproof varnish; the second he partly remedied by furnishing the pattern roller (a cylindrical block in reality) with colour from a short endless blanket, over which the colour was evenly distributed by two plain rollers—one, the furnisher, working partly immersed in the colour, and the other, the distributor or spreader, simply pressing against the blanket. Further, by multiplying the number of rollers round the central bowl, he contrived to print several colours at once.

These and other of Burch's improvements made it possible not only to print surface rollers, with more or less success by themselves, but also to associate them with engraved copper rollers in the same machine, and thus print both styles at the same time—a combination of relief and intaglio printing largely practised at that period by Peel, of Church Works, and occasionally even to-day for special patterns.

With the exception of a few minor improvements—such as the introduction of stereotyped relief rollers and little matters relating to the adjustment of the various parts of the machine—Burch's principle is still in use for surface printing.

The following three diagrammatic sketches will sufficiently illustrate the principle of the different arrangements used by Ebinger, Burch, and Gadd & Hill respectively.

In fig. 17 (Ebinger's), A is the pressure cylinder wrapped with a woollen blanket E; B is the pattern roller or cylindrical block; C the colour furnisher wrapped with cloth; D the colour box; and Z the cloth. All the parts are adjustable to each other. In fig. 18 (Burch's), A, B, C, and D refer to the corresponding parts in fig. 17; E and GG are carrying rollers for the colour-furnishing blanket I; F is the spreading roller or distributor; X an endless blanket passing continuously round A; Y the back grey to preserve the blanket from colour; and Z the cloth to be printed. The rollers E, GG, and F are all adjustable by screws; E for regulating the quantity of colour supplied to I; GG for varying the area of contact and the pressure between B and I; and F for taking up the position best suited to its purpose when the other rollers are altered. Fig. 19 represents, in a somewhat exaggerated manner, the disposition of the rollers round the cylinder of an eight-colour surface printing machine made by Gadd & Hill of Salford. Only two rollers are shown fully fitted with their colour boxes, etc.; but the other six are arranged in practically the same way, with, of course, slight variations in detail, according to the different positions they occupy round the cylinder. Fig. 19 is, to all intents and purposes, identical with fig. 18, except that it displays more rollers, and that the spreading or distributing-roller F in the latter is replaced in the former by a blade of metal (or of wood) called a "doctor," which rests very lightly upon the travelling colour blanket, and equalises the colour it brings forward from the furnisher by a slight lateral to-and-fro movement, the effect of which is to spread the colour across the width of the blanket as it escapes under the doctor. By means of this combination of travelling

blanket and traversing doctor it is very easy to produce rainbow, *ombré*, or *fondu* effects, similar to those obtained by the rainbow method of hand block printing. For this purpose it is only necessary to divide the colour box into as many compartments as there are colours desired, fill each one with its particular colour, and proceed as for ordinary printing; the movement of the doctor has sufficient amplitude to blend the edges of the several stripes of colour together into one continuous series of vari-tinted bands across the full width of the colour-furnishing blanket, so that no part of the printing roller is deprived of colour.

Notwithstanding the many improvements effected in the surface printing

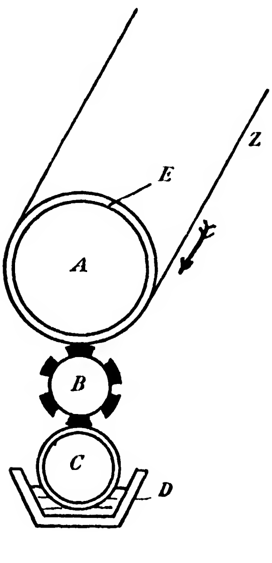


Fig. 17.

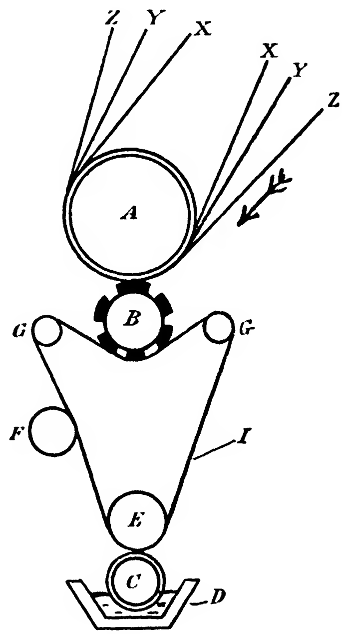


Fig. 18.

Types of surface or peg printing machines.

machine, it has never come into general use for textiles, nor has it even replaced, to any appreciable extent, other methods of block printing.

The advantages it has, in being capable of printing multicolour patterns at one operation in a continuous manner, with perfect repetition of the design, and at the same time allowing of a high rate of production, are more than counterbalanced by the technical difficulties it gives rise to in practice. These may be summed up as follows:—

Firstly, being a complex machine, it requires much more than ordinary supervision on the part of the printer, and consequently the risks of faulty work are increased. Secondly, unlike ordinary block or perrotine printing, the surface roller can only receive one application of colour at each revolution, and therefore is more liable than they are to both take it up and transmit it unevenly; moreover, the constantly varying tension of the endless colour-carrying blankets exerts considerable influence on the regularity of the resulting print; and when it is considered that the adjustment of each blanket requires the alteration of either the doctor or one or more of five rollers, it is evident

that the printer has his hands full. Thirdly, it is *impossible* to obtain from surface rollers a perfect impression of the pattern. This last is an inherent defect in the process, and is due to the fact that when colour is applied from a *rounded surface* to one not perfectly absorbent, it gets squeezed backwards into a little heap, which in surface printing spreads out somewhat beyond the lower boundaries of the engraved objects, and gives them the appearance of having been smeared. This is not always very noticeable, but it is always liable to occur, and it constitutes one of the greatest practical objections to the employment of surface printing for textiles.

At the present time surface printing machines seldom find application in

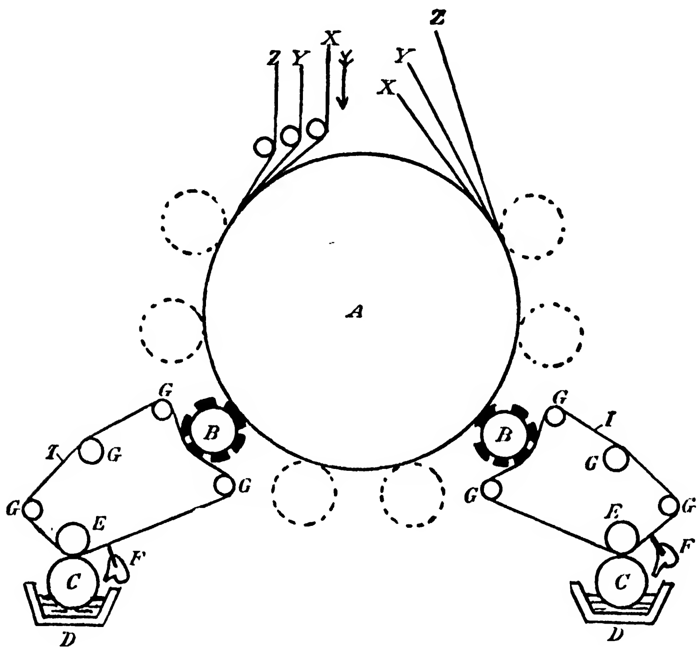


FIG. 19.—Another type of surface or "peg" printing machine.

the calico-printing industry except on rare occasions when special effects of solid, outstanding masses of opaque colour, otherwise unattainable, are desired. On the other hand, they occupy an important place in the printing of oilcloth, linoleum, yarns, and wall-papers, and are also used to some extent in the printing of certain classes of woollen goods. In each of these cases comparatively coarse, heavy patterns, large in scale, are for the most part used; and as crispness of definition is not essential to their success, the chief defect of surface printing is, within certain limits, of no account.

Up to eighty years ago an enormous number of inventions and improvements had been made in block printing, with the object of stemming the steadily increasing popularity of Bell's cylinder printing machine. Various schemes of multicolour printing were tried, in which use was made of travelling sieves, of ingeniously constructed mechanical blocks, capable of being enlarged or diminished in area, or of bringing forward in turn each of the separate parts of the design, and of numerous other modifications of the appliances and

processes of hand printing. None, however, except the perrotine, the surface printing machine, and ordinary hand block printing have survived, except in rare instances, for the cheapest class of felt and carpet printing. All attempts to keep pace with the rapid development of cylinder printing from engraved rollers were in vain, and gradually block printing declined in importance, until by about 1870 it had fallen into almost complete disuse. But hand block printing was never entirely superseded by any form of machine for certain classes of work, and during the last fifty years the increased interest taken in all handicrafts, due primarily to the magnificent work of William Morris and his collaborators, has resulted in its revival, and in that of the patterns for which it is peculiarly adapted. At the present time many of our foremost artist-designers are engaged in designing patterns for block printing, and it is now no uncommon thing for the best and most celebrated house-furnishing establishments to devote a whole window to the display of fine specimens of block-printed cretonnes, chintzes, bedspreads, table-covers, curtains, and other articles of a decorative nature.

(3) STENCILLING.

Although stencilling on textiles is an old process—it was employed tentatively in the early days of calico printing in Europe—yet until a few years ago it was scarcely known in this connection, and was almost unrecognised as suitable for anything but the marking of bales, cart-sheets, and other work of a like rough nature. It is only within the last forty-five years or so that its possibilities as a mode of *decorating* textile fabrics have been fully revealed by the publication of works on Japanese art, and by the exhibition of specimens of Japanese work. Even yet it has not received from calico printers that amount of attention to which its merits would seem to entitle it; but this, perhaps, is not surprising, considering that for a long time by far the greater number of available examples of stencilling were the work of the ordinary house decorator and plumber, in whose hands its finest qualities were lost, and who, instead of turning its limitations to account, emphasized them to the point of ugliness. It is not to be wondered at, therefore, that stencilling came to be generally regarded as a mere makeshift for the cheap ornamentation of wall spaces and dado borders, and that consequently it was, until recently, neglected by textile printers, whilst other methods of printing advanced. During the last few years, however, many of our best designers have recognised its capabilities, and have demonstrated by their excellent work that, properly employed, it affords a cheap, ready, and efficient means for the decorative treatment of almost every kind of textile material—cotton, linen, wool, jute, silk, and velvet. In England stencilling on these various fabrics is usually confined to hangings, curtains, bedspreads, table and cushion covers, and canvas for wall-coverings and friezes, etc., etc.; but that it is not restricted to the execution of these comparatively large-scale patterns is shown by the delicate designs stencilled by the Japanese on fine silk and cotton muslins, suitable for dress goods.

As compared with block printing, stencilling offers much greater latitude to the designer in the planning of his ornament. The pattern may be intricate or simple; delicate or broad; in fine line or mass, or both combined; and in either flat or gradated and broken tints. The facility with which fine line and mass can be produced from one stencil plate, and the ease with which two or more different colours can be blended in one object, constitute the chief technical advantages of stencilling over block printing. Against these must be put the impossibility of cutting a perfect circle or any other complete outline on a

stencil plate. A spot merely requires a hole to be punched right through the plate, but if a complete circle were cut the inside would drop out at once, leaving a spot; similarly with all other uninterrupted outlines. To prevent this, the outlines of a pattern must be broken at convenient points, by being only partially cut, the uncut or reserved portions—known as *ties*—serving to support the inside parts by connecting them with the rest of the reserved portions, or the body of the plate—see fig. 20, *C*, where the circumference of the circles are interrupted at every point of intersection.

Stencil plates are merely sheets of paper or thin metal, with perforations arranged to form a pattern. They are laid on the work, and colour is brushed through their cut-out parts on to whatever material shows beneath them, thus producing a coloured pattern corresponding to the shape of the perforations. Ties are not only used for outlines, but must be freely introduced, for strength, wherever long lines, extended spaces, or intricate patterns are cut, otherwise the plate will be too fragile, and apt to lie unevenly on the work, and thereby give rise to faulty execution. Although an unbroken outline cannot be *stencilled*, it may be *reserved* or left uncut in cases where both ground and pattern are cut out on one stencil, or where two or more plates are employed for the realisation of a multicoloured design—in which cases it (the outline) appears in the original colour of the material to be ornamented. This method of working is illustrated roughly in fig. 20, *B*, where a continuous white outline is obtained by cutting two separate stencil plates, one for the black parts and the other for the shaded parts.

In some of their best textile work the Japanese cut their paper stencils with such exceeding delicacy that the ties left are not, by themselves, sufficiently strong to hold the plate together. They therefore cut two identical stencils at the same time from a doubled sheet of paper, and afterwards glue them together with a layer of raw silk threads between them. These threads, which extend over both the cut and uncut parts of the plate, afford the necessary support to the pattern, and as they always lie a little distance above the surface to be decorated, and are so thin, they easily allow the colour to spread under them, and do not in any way affect the ultimate result, except to improve it. Marvellously delicate effects are obtained in this way, but it is open to question whether such refinements of process do not exceed the proper limits of stencilling.

The best modern designers, so far from being hampered by the necessity for ties, frankly admit their limitations, and make effective use of them as integral parts of the design. They avoid the clumsy and arbitrary breaks of line, so common in older work, by ingeniously arranging the ties to suggest the veining and doubling over of leaves, the twisting of tendrils, the junction of flowers and leaves with stems, the folds of drapery, and a hundred and one other natural effects.

The character of a single-colour pattern may be varied in several different ways at very little cost. The background may be cut out, leaving the uncut portions of the plate to represent the pattern; conversely, the pattern may be cut out, leaving the ground in reserve, when it will appear in the natural colour of the material under treatment; or by applying different colours separately, and blending them on the work, with a stroke of the brush, before the plate is removed, a great variety of broken or gradated colour effects may be easily obtained from one stencil—effects quite beyond the power of either block or machine printing to attain.

The same rules that govern the repeats of patterns in block printing apply equally in stencilling, and similar means may be employed to mask the prominence of awkward repeats. Generally speaking, every stencil plate must con-

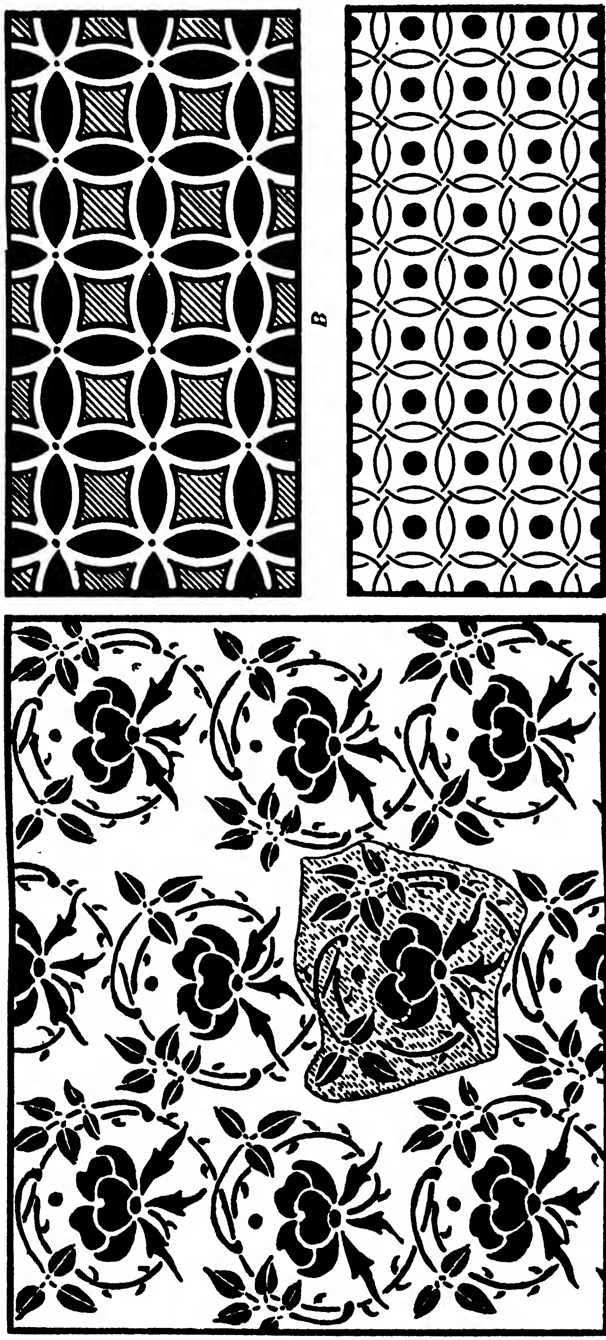


FIG. 20, A, B, C.—Stencil patterns.

tain at least one full repeat of the design; but in the case of certain geometrical, and all "turn-over," patterns only half a repeat need be cut, the other half being added on the work by reversing the plate. Unless the pattern be very large or intricate it is better, however, to cut the full repeat; for in reversing the plate it requires very careful cleaning, and frequently, too, the previous impression must be allowed to dry before the second half can be stencilled. The turn-over pattern is a device borrowed from the weaver. It is constructed on straight or waved parallel vertical lines, and being of necessity symmetrical, it is obvious that if the stencil plate contain only half the pattern, the whole can be completed by turning it over and stencilling through the back. The same principle can also be applied in stencilling to unsymmetrical patterns, as shown in fig. 20, *A*, where the shaded portion of the design represents the stencil plate used, the black parts being cut out.

In patterns of two or more colours a separate stencil plate is required for each distinct colour. It is possible, with care, to obtain a two- or even a three-colour pattern from one plate by applying the particular colours to certain parts of it, but it is a risky method, and one seldom resorted to in practice, separate plates for each colour being almost invariably preferred. In an elaborate pattern, requiring several plates for its realisation, one plate may be schemed to make good the ties of another; but, as a rule, the most artistic results are obtained by allowing the ties to be seen, and by utilising them for the twofold purpose of strengthening the plate and of serving as an essential feature of the design.

All stencilled patterns ought to be complete as stencilled; if they require any subsequent re-touching by hand, the design is either unsuited to the process or its planning is defective.

Unlike other methods of textile decoration, stencil work permits of the pattern being carried out in almost any kind of colour. For heavy woollen goods, velvets, jute, and buckram, which are destined to serve as hangings, wall-coverings, and decorative panels, oil colours are frequently used, brushed lightly over the surface of the material, so as to retain its "clothy" appearance as much as possible. For cotton, linen, silk, and lighter goods generally, either water-colours or the ordinary dyestuffs may be employed, according to the purposes for which the work is required; the former in special cases, and the latter for such articles as tablecloths, curtains, bedspreads, and the like—all of which require to be fast to washing. Work executed in oil or water colours is finished when dry, but when dyestuffs are made use of the goods must, of course, go through the usual operations necessary to their proper fixation.

A stencilled pattern, though quite different in character from, is quite equal in its way to, a block print. It possesses similar qualities of colour and breadth, and is subject in all-over patterns embodying long unbroken lines, or long stretches of unbroken colour, to the same misfitting of the repeats. Whatever beauty some people may claim to find in such "misfits," a practical stenciller always tries his utmost to avoid them by arranging his design to repeat at the ties. It is not always possible to do this, however; hence their occasional appearance in even the best work. On the whole, the most successful patterns for stencilling (and also for block printing) are those in which no tight-fitting joints are necessary, *i.e.* patterns made up of detached units—powdered patterns, with an unbroken space of background surrounding each repeat.

Stencil plates cannot be manipulated quite so quickly as blocks, and, in consequence, for the commercial production of large quantities of printed textiles, stencilling is not cheaper than block printing. On the other hand, the low cost of the materials and the rapidity with which the plates can be cut enable it to be profitably employed in the execution of small orders, for

which the expense of block cutting alone would be prohibitive, as, for instance, when, as frequently happens in high-class house furnishing, a small quantity only of a special pattern is required to complete a scheme of decoration.

The making and using of Stencil Plates.—As above noted, stencilling is not strictly speaking a printing process. Colour is applied to the material to be decorated, not by impression, as in printing, but by being brushed or sprayed [1] through the interstices of a pattern cut out in waterproof paper or thin sheet metal.

Stout cartridge paper or two-sheet Bristol board is usually preferred for stencil plates. Whichever is selected must first of all be saturated thoroughly with either boiled or raw linseed oil. When it has absorbed as much as it will hold it is wiped dry, and the last traces of superfluous oil removed by pressing it for some time between two sheets of similar paper. Freshly prepared in this way, cartridge paper is tough, supple, easy to cut, and sufficiently transparent to permit of a tracing of the design being made upon it directly; but if kept for any length of time it becomes hard, brittle, and opaque, and dark in colour.

The cutting out of the pattern is done with a sharp-pointed knife, and is best accomplished on a sheet of plate-glass, the hard, polished surface of which, by offering no obstruction to the passage of the knife, allows it to cut cleanly, smoothly, and regularly through the paper, and ensures not only more accurate work than could be obtained on a wooden table, but also effectually prevents the raising of burrs or rough back edges on the underside of the stencil. After cutting, the plate is made impermeable to moisture by coating it on both sides with a waterproof varnish. A solution of shellac, or the tougher resins, in methylated spirits or naphtha, answers this purpose; it dries quickly, leaving a hard, durable surface, easy to clean, and not readily affected by the colours.

Stencil plates may also be made of thin sheet copper or zinc, but they are dearer than those in paper, less easy to cut with accuracy, and, in any but small sizes, more difficult to handle in practice. Whilst they are superior to paper in so far as durability of material is concerned, their thinness has the disadvantage of rendering them more liable to damage in the course of working. The slightest blow or a fall is quite enough to cause dints or creases in a metal stencil—defects which, by preventing it from lying flat on the work, render it temporarily useless. Moreover, these defects, as is well known, are difficult to remedy, some experience of sheet-metal work being necessary to flatten out a locally warped or creased plate without causing it to spring in some other part. Generally speaking, paper stencils are the best for all ordinary purposes. Their initial cost is very low, and they are very easy to duplicate if they happen to get torn. Another great advantage they possess is that, owing to their transparency, each of the separate colour parts of a multicolour pattern, together with the gauge or pitch marks, can be traced directly on to the stencil plates, thus obviating any mistakes that might arise in transferring separate tracings to separate plates, and making certain, without any preliminary trial, that every colour in the design will register perfectly.

The *modus operandi* of stencilling is very simple. The plate is laid perfectly flat on the material to be treated, and suitably thickened colour is then brushed through its perforations with a hog-hair brush. On lifting the plate the pattern appears on the cloth as a coloured silhouette, corresponding with the cut-out parts of the stencil. Different effects may be got according as the colour is brushed, dabbed, sponged, or sprayed through the stencil, and still others may be obtained by placing different colours on different parts of the stencil, and

[1] For spraying, a special apparatus is made by The Aerograph Co., Ltd., of Holborn Viaduct, London. The flow of colour from the nozzle is under perfect control and can be regulated at will so as to obtain any desired degree of gradation.

then blending them together with a sweep of the brush. In this way each repeat of the pattern will vary in tone somewhat, but will still retain the general appearance of the others.

In stencilling patterns of two or more colours the same procedure as that adopted in hand block printing is followed. The cloth is stencilled throughout in one colour first, then dried, and the others added in like manner. If desired, it is obvious that every repeat may be coloured differently, and this variation is frequently made use of in stencilled wall-hangings and papers—that are executed for special schemes of house-decoration—for the express purpose of getting lighter colours in dark corners.

No definite rule can be laid down as to the consistency of the colour nor the amount to use, but it should be thick enough not to run, and applied in sufficient quantity to cover the material well without spreading under the uncut or reserved portions of the stencil.

Screen Printing.—Under this designation an interesting method of decorating textile fabrics has, of recent years, attained to considerable importance. It is not really a *printing* process at all, but purely and simply an improved method of stencilling, which, by dispensing entirely with the necessity for "ties," gives the designer a much wider scope in the planning of his pattern than is afforded by the older methods.

In screen printing the ordinary stencil plate is replaced by a tightly stretched drum or screen of thin silk gauze on which the pattern is *painted* in such a way that the *unpainted* parts correspond to, and fulfil exactly the same function as, the perforations in a stencil plate, *i.e.* they allow colour, properly applied, to pass through them freely, and thus to be transferred to any fabric placed beneath.

The principle applied in making screens or silk stencils is analogous to that employed by the Japanese in strengthening and supporting the fragile ties of their delicately cut paper stencils (page 42). The apertures of the screens are spanned by permeable silk gauze ; the perforations of the Japanese paper stencils are spanned by what may be regarded as a fine grating of raw silk threads.

Screen printing is carried out on wooden or concrete tables similar to those used for block printing, but generally of lighter construction and preferably of much greater length. The length of the table is an important factor in obtaining an economical rate of production. If a short table is used, especially with a large screen, the output is considerably reduced owing to the loss of time entailed in drawing a fresh length of cloth over the printing table at frequent intervals. If possible the table ought to be as long as the piece to be printed. Tables twenty and thirty yards long are not uncommon.

The Making of Screens.—The stencils or screens used in this process resemble shallow trays in form. They consist of fine bolting silk (such as is used by millers) stretched tightly over, and cemented to, strong wooden rectangular frames which are, usually, 6 to 8 inches wider than the material to be printed, and also 6 to 8 inches longer than the vertical repeat of the pattern. A separate stencil is required for each colour in a multicolour pattern.

The actual stencil is made by placing the silk-covered frame over the design and tracing, with pencil, the outline of the pattern, or one of its colour units, on the transparent stretched silk. Those parts of the pattern (outside the outline) which are *not* to be printed are then painted out, by hand, with a waterproof varnish, or a cellulose lacquer, which completely fills up the mesh of the silk and renders it impervious to colour. The size of the screen ought to be such as to allow of a broad band of solid lacquer being painted

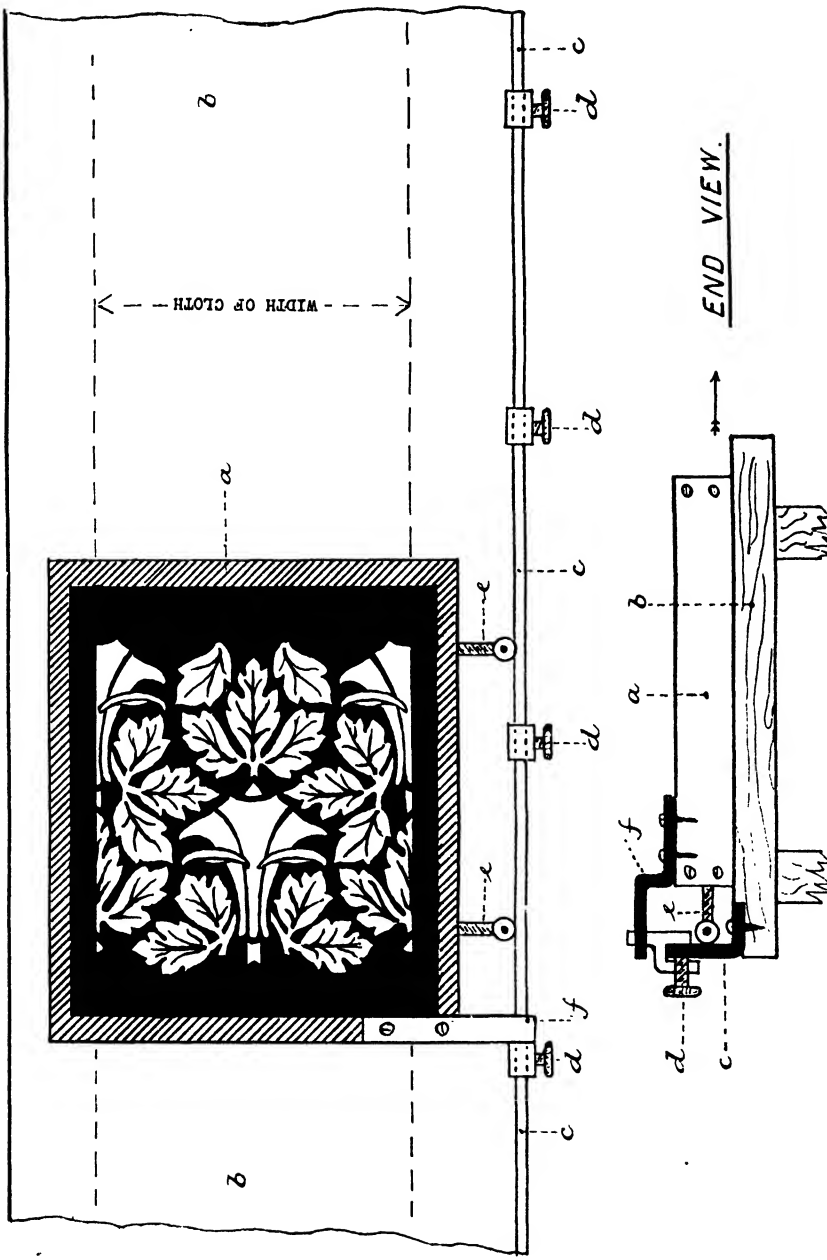


FIG. 21.—Screen printing.

round the entire pattern, as shown in fig. 21, in which the solid black[1] represents the *reserved* or painted-out portions of the pattern, and the white the actual pattern which will appear in colour when the stencilling is carried out.

A relatively slow drying lacquer is the best to use for screen painting—one which is not completely dry until about an hour after its application—and it ought to work easily under the brush and give a tough pliable film capable of withstanding both the action of water and the friction of the squeegee used for stencilling the colour through the unpainted portions (or pattern) of the screen.

Screen printing is carried out in much the same way as is ordinary stencilling, except that the colour is applied not by a brush but by means of a rubber or wooden squeegee of wedge-shaped section, tapering from $\frac{7}{16}$ inch at the top to $\frac{3}{16}$ inch at the bottom or working edge and almost as long as the stencil. The screen being placed on the cloth, drawn over the table, colour is poured over one of its solidly-painted borders, and is then rubbed across and through the *unpainted* portions in one or two strokes of the squeegee. On lifting the screen the pattern appears on the cloth as a coloured silhouette corresponding in shape to the unpainted parts of the screen.

For most purposes it is sufficient simply to lay the material to be " printed " on the bare table ; but in the case of particularly delicate fabrics, such as tulle, etc., the position of which, on the table, is liable to be disturbed by the slightest touch, or even by a draught, the printing table is frequently covered with waxed paper or cloth to which the fabric is caused to adhere by gentle pressure in the well-known manner employed in the process of printing textiles by lithography. In this way the fabric is prevented from moving when the screen is lifted and moved forward to print the next repeat of the pattern.

The colours used for screen printing call for no particular description. In general composition they are identical with those used for block printing, but thinner in consistency, so as to pass easily through the meshes of the stencil. At the same time they must possess sufficient body to print smartly without " bleeding " beyond the limits of the pattern.

Registration or Fitting of Screens.—Of the various devices in use for ensuring the correct registration of the " repeats " in a sequence of printings, the one illustrated in fig. 21 is as convenient as any for goods of normal width.

Along one side of the printing table (*b*) a guide rail (*c*) of well-trued angle-iron is fitted. To this rail adjustable stop clamps (*d*) are screwed at intervals corresponding exactly with the length of the vertical repeat of the pattern carried by the screen frame (*a*). On one side of the screen frame (*a*) a gauge (*f*) of strip iron is screwed, and this gauge is brought up close against each of the stop clamps (*d*) in turn as the screen is lifted and moved forward for another printing. The adjustment of the screen in the direction of its width, or side repeat, is effected by means of two regulating screws (*e*) fitted into the frame of the screen, and serving to determine the distance of this latter from the guide rail (*c*) as shown in fig. 21.

In some cases the iron rail (*c*) is replaced by a straight wooden rail pierced with holes, at suitable distances apart, into which pegs are inserted to act as stops instead of the afore-mentioned screw clamps.

For unusually large screens both sides of the table may be fitted with the foregoing means of adjustment.

[1] In practice the lacquer used is not black, but a light shade of any colour—sometimes transparent.

Designs Suitable for Screen Printing.—It is obvious, from the method of making screens by painting round the pattern, that the designs most generally useful for screen printing are those planned on broad conventional lines, with well-defined colour masses and free from fine line detail *in colour.* Fine lines may, of course, be painted on the screen and will then appear in white after stencilling; but it is very difficult, and a slow process, to leave unpainted, delicate, ornamental details made up of fine lines, dots, circles, etc. which are required to be stencilled *in colour.* Such delicate ornamental motifs in line may, however, be obtained by a process of resisting recently published by the I. G. Farbenindustrie.

Screens Made by "Resisting."—By this method the pattern is carefully painted on the silk screen with a solution of silicate of soda (90° Tw.) which may be tinted with Rhoduline blue G.O. for sightening purposes. After drying, the whole surface of the screen is painted over with the following lacquer, using a broad brush:—

650	grms.	Screen lacquer L.P. (I. G. Farbenindustrie).
200	,,	Anon.
150	,,	Methylated spirit.
1000	,,	

The lacquer is allowed to dry thoroughly and the screen is then washed with warm water to dissolve out the silicate of soda, the "resisted" portions being gently brushed at the same time with a soft wire brush to facilitate the removal of the lacquer. Fixation of the lacquer is prevented wherever it falls over the silicate of soda; hence, on washing and brushing, it comes away, leaving the pattern clear.

For screen printing with strongly alkaline colours it is necessary to use fine wire gauze in place of bolting silk, which latter is rapidly destroyed by alkalies.

Screen printing is a much more comprehensive process than is ordinary stencilling. The structure of the screens or stencils, consisting as it does of a strong and continuous web of silk unbroken by perforations, allows of patterns of almost any size being handled with ease and certainty. The fact, too, that the absence of ties liberates the designer from the restrictions imposed by the conditions of stencilling, gives him almost unlimited freedom in the planning of his ornament and enables him to introduce decorative features—such as circles and other unbroken outlines—which are impossible of realisation in ordinary stencilling. This absence of ties and the relative strength of the screens constitute, perhaps, the most important and characteristic advantages of screen printing; the first permits of patterns of almost any style being produced by a method of stencilling, and the second allows of patterns of almost any dimensions being dealt with without any fear of the stencil falling to pieces.

In breadth of effect, decorative value and richness, transparency and purity of colour, a screen print compares favourably with a good block print, and for a limited quantity of exclusive styles it is the cheaper and quicker process. Screens are much more quickly painted than blocks are cut, but they are of course not nearly so durable and, therefore, where large quantities of a pattern of normal dimensions are required, block printing is the more economical and convenient process to employ.

For special styles of decorative fabrics—such as the large printed panels which consist of a design complete in itself (without repeats) and enclosed within an ornamental border—screen printing is particularly useful. Hitherto

panels of this description, of large size and employed like tapestry for wall hangings, have been printed either by lithography from large zinc plates or by block printing. Both these methods possess inherent drawbacks. Lithographic printing on textiles is cheap, but it yields flat, thin colours which are difficult to keep even in shade. Hand block printing, on the other hand, leaves little to be desired in the way of fine effect, but it is expensive for this large-scale work because the size of the design requires several blocks to be cut for each colour unit, as described under the heading "Block Cutting on Wood" (p. 22). Both these drawbacks are overcome by the use of screens, which are quickly made, as quickly applied, and may be of any size capable of being handled with ease. Screens measuring 6 feet long and 4 feet wide are reported to be in current use and, possibly, still larger ones are not unknown.

Stencilling Machines.—Only two stencilling machines have ever been used to any extent in calico printing,—one known in its final form as Monteith's Press, and now obsolete; the other a modern machine, invented by S. H. Sharp for printing metallic powders, etc.

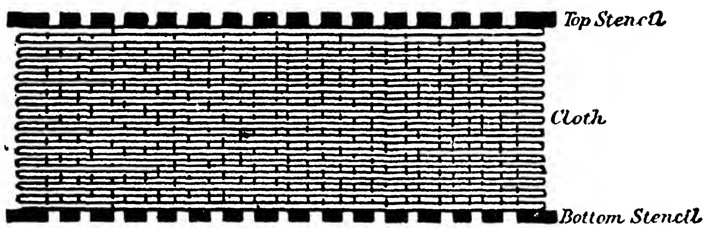


FIG. 22.—Illustrating the principle of Monteith's press.

Monteith's press was used for the production of "bandanas," a peculiar kind of handkerchief, with a pattern consisting of spots and other simple objects in white or yellow on a dyed ground, generally of Turkey red or of Indigo. Briefly described, the process was as follows:—Several pieces of cloth, folded to the requisite size, were tightly compressed in a modified hydraulic press between two leaden stencil plates pierced with identical patterns, and arranged so that their perforations lay exactly over each other; a liquid discharging agent—a solution of bleaching powder—was then forced through the whole by means of a hydraulic pump, and, following the line of least resistance in its passage through the cloth, it only destroyed the colour in those portions lying immediately between the perforations in the two stencil plates. A full description of Monteith's press may be found in Persoz's *Traité de l'impression des tissues*, but fig. 22 illustrates the principle made use of. The dotted lines indicate the direction taken by the discharging agent; the thin horizontal lines, the folds of the cloth; and the heavy broken lines at the top and bottom of these latter, a section of the two identical stencils, showing how their respective perforations must correspond.

Work done by this process was chiefly characterised by its coarseness of execution; and although it imitated native Indian bandanas fairly well, it was much inferior in all other respects to the work of contemporary block printers. Owing to the fact that no amount of pressure could entirely prevent the discharging agent from spreading by capillary attraction into the surrounding ground colour, it was impossible to employ anything but spots or the simplest

clear-cut masses in the designs, and even then the raggedness of their edges was always more or less in evidence. The whole process was exceedingly cumbersome, and its only resemblance to stencilling lay in the use of the pierced leaden plates—certainly not in the effects produced, which resembled poor block prints more than anything else.

The continuous stencilling machine, patented by S. H. Sharp in 1894, is entirely free from the defects of Monteith's press, and is applicable to a much wider range of designs, including stripes, which are impracticable in ordinary stencilling, on account of the difficulty of hitting off the repeats exactly. Sharp's machine consists essentially of the following parts, geared to work together by power, and arranged as shown in figs. 23 and 24 :—

A is an endless metal stencil, carried by the plain rollers I, I′, one of which (I′) is adjustable ; B an iron cylinder, also adjustable ; C a fixed colour box,

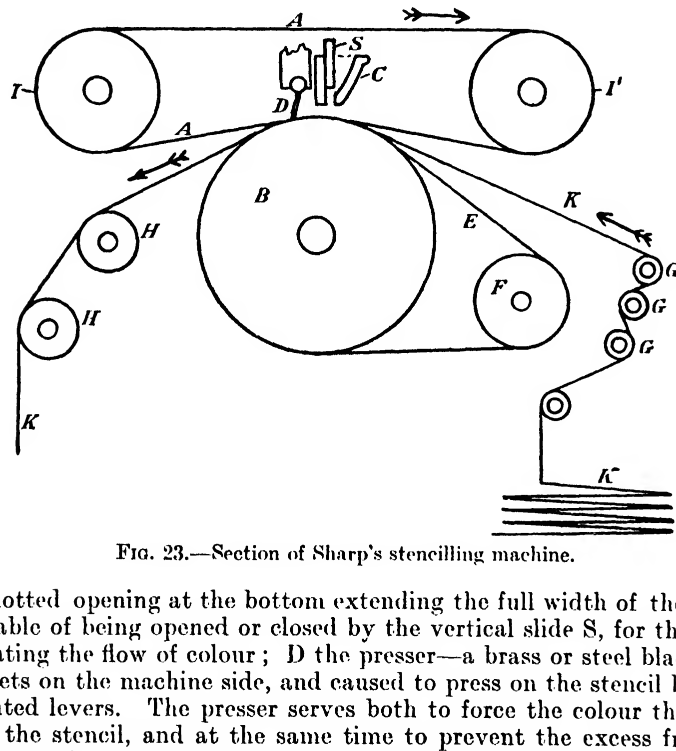


FIG. 23.—Section of Sharp's stencilling machine.

with a slotted opening at the bottom extending the full width of the machine and capable of being opened or closed by the vertical slide S, for the purpose of regulating the flow of colour ; D the presser—a brass or steel blade carried in brackets on the machine side, and caused to press on the stencil by springs or weighted levers. The presser serves both to force the colour through the holes in the stencil, and at the same time to prevent the excess from being carried forward. E is an endless woollen blanket circulating round the cylinder B and the adjustable roller F ; G, G, G, tension rails for keeping the cloth K tight and free from creases ; H, H, drawing rollers, covered with sandpaper, or fine pins, for carrying forward the cloth, after printing, to the drying chamber, where it is suspended on rails until dry.

The ordinary stencil used in this machine is simply a thin sheet of steel or brass, brazed at the ends to form an endless band, and perforated with any desired pattern made up of *detached* ornamental units. For continuous stripe patterns a different arrangement is necessary. When these are to be printed the plain rollers I, I′ are replaced by corrugated ones (X, X′, fig. 24) made up by slipping large and small slotted iron discs on a tongued spindle, and tightening them up by means of a nut on the end of the latter. Guide

rollers (Y, Y, fig. 24), similarly constructed and of the same pitch, are also added, and, instead of the stencil, a series of endless steel bands or tapes are employed, varying in width according to the sort of stripe required. The corrugations in the rollers must, of course, correspond in width to the width of the tapes which work in them, as otherwise the stripes printed would vary in thickness. By this ingenious modification of stencilling it is possible to print stripes showing absolutely no repeat. The patterns may be varied by combining wide and narrow bands, the corresponding guide and bearing rollers being built up of discs of various thicknesses. In fig. 24 the colour box C is not shown, but it occupies the same position as in fig. 23.

The operation of printing is carried out as follows:—First the end of the cloth (K) is inserted between the stencil (A) and the bowl (B); colour is then allowed to run on to the top of the stencil, and the machine is set in motion when stencil, bowl or cylinder, and cloth all move together in the direction indicated by the arrows. During this movement the colour is carried forward against the presser (D), which forces it through the pattern on to the cloth beneath, and at the same time scrapes off the excess from the plain or uncut portions of the stencil, leaving it quite clean. If this excess of colour were allowed to remain it would spread through the pattern to the underside of the stencil, and, at the next revolution of the machine, would be transferred to the cloth and produce faulty work. As the cloth emerges from beneath the stencil it is led over the draw-rollers (H, H), which continue to carry it forward into the drying chamber as long as the machine is in motion. The drying chamber is situated close to or below the machine, and consists of a steam-heated brick room, furnished near the top with wooden rails, over which the cloth is hung in long loops, so that its printed side never comes into contact with anything until it is perfectly dry.

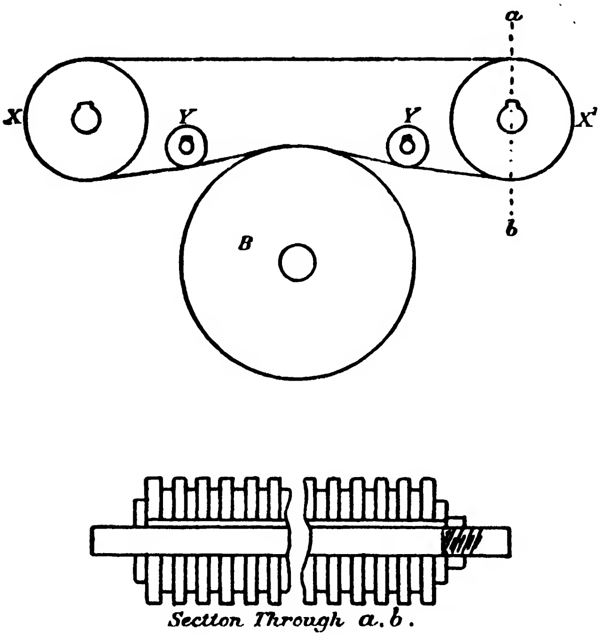


FIG. 24.—Section of Sharp's stencilling machine.

The chief use to which this machine is put is for the printing of metallic powders. On an ordinary printing machine metallic powders are difficult to work, as they tend to fill up the engraving of the rollers and frequently give rise to thin, bare impressions; but in Sharp's machine neither of these defects is possible, and consequently the resulting print is full and rich in colour, and, after drying and calendering, exhibits a brilliant metallic pattern. The metal, being mixed with an oil-varnish, adheres tenaciously to the cloth, and is not only fast to washing, but also remains untarnished for a very long time, even when exposed to the action of town air.

(4) PLATE OR FLAT-PRESS PRINTING.

Before the introduction of the roller printing machine the only means available for the reproduction on textiles of the most delicate line and stipple designs was by printing them from flat copper plates, engraved by hand with a burin or steel graver in the ordinary well-known way.

Originally the process was carried out exactly as for the printing of engraved pictures, and, according to Girardin, was first practised on calico in 1770 by Bell, the inventor of roller printing. The plate, engraved with the pattern, was entirely coated with printer's ink, rubbed well into the engraving with a soft pad; the excess was then removed from its plain surface by first wiping several times with a cloth, and finally with the ball of the hand until no part of it except the engraved lines retained the slightest trace of ink. A piece of cloth was then laid over it and the two together passed through a heavy cylinder press, the pressure of the steel bowls of which forced the cloth into the engraving of the plate, and thus caused the pattern to be transferred to it. The process was slow, and, from its nature, it is obvious that only small articles—such as handkerchiefs—could be printed, as repeats were impossible to fit, and long lengths of cloth were impracticable to handle.

In the flat-press machine, which is constructed on similar lines to the modern lithographic machine, the latter defect is overcome, but the difficulty of the repeats is still such that continuous designs are never attempted, and consequently the flat-press is restricted to the printing of patterns that are either made up of detached objects or sprays, or that are complete in themselves without repeats—as, for instance, tablecovers, panels, or handkerchiefs. Practical difficulties also prevent the flat-press from being used for more than one colour, though it is possible that if the cloth were backed with a stout, waxed paper support to prevent it stretching, it might be printed in several colours, in the same way that posters are printed on Prebay's continuous lithographic machine.

In the flat-press machine the engraved copper or steel plate is mounted on a heavy iron carriage, which moves to and fro in such a way that the plate, when inked, passes under and in contact with a heavy woollen-covered iron cylinder, between which and the plate the cloth to be printed passes. As the carriage moves forward the cylinder revolves and presses the cloth into the engraved pattern on the plate, thus making the desired impression. On leaving the cylinder, and whilst still moving forward, the whole plate is re-inked automatically, the excess of ink being then removed from its surface by a steel doctor or blade, which is arranged to bear upon it during the return journey of the carriage to the back of the machine. During this return journey the plate re-passes under the cylinder, but out of contact with it. On regaining its original position a system of cams comes into play, and raises it sufficiently to make contact again with the cylinder at its second forward movement, and so print a second length of cloth. In this way the machine works continuously, printing the cloth in an intermittent manner. As the cylinder remains stationary, except when in actual contact with the travelling plate, it allows of the second impression being commenced where the first leaves off; but as the exact junction of the repeats cannot be relied upon in delicate patterns, and as coarser patterns are better and more cheaply executed by block printing, the flat-press is still only made use of for those finely engraved powdered and bordered patterns which at the time of its invention it was impossible to execute by any other means.

At the present time flat-press printing is practically obsolete in most

countries, except for, perhaps, a few fancy articles on satin, for which there is an occasional slight—very slight—demand. In Switzerland, however, it is still used to some extent for the production of a special style of handkerchief with a finely engraved border and a floral centre—the latter being filled in by block printing after the border has been printed on the flat-press.

(5) MACHINE, ROLLER, OR CYLINDER PRINTING.

Machine printing is the name generally applied to the process of printing from engraved copper rollers, as distinguished from hand block printing, perrotine printing, surface printing, and stencilling. It is at once the most important, most productive, and most comprehensive of all the various methods of ornamenting textiles ; and by its means almost any style of design on almost any fabric can be rapidly reproduced in from one to sixteen colours at a single printing. Compared with stencilling, hand block, and perrotine printing, the output from a cylinder machine is enormous, under favourable conditions as much as 18,000 yards of cloth being printed in one colour, or 8000 to 9000 yards in twelve colours, per working day. Moreover, the technical excellence of the work so obtained is not in any way sacrificed to the high rate of production.

The Roller Printing Machine.

The invention of roller printing is generally attributed to Bell, a Scotchman, who patented it in 1783, and who first employed it with practical success at the works of Livesey, Hargreaves & Co., near Preston, in 1785.

It is an open question, however, as to whether or not he was the actual originator of the idea, for O'Neill quotes two previous patents which seem to prove that a considerable amount of work had been done on similar lines at a much earlier date. In 1743 Keen and Platt patented a three-colour machine with a separate pressure bowl to each roller ; and in 1772 Aitkin patented a single-colour machine in which three bowls or rollers of sycamore worked one above the other, in slots in the sides of the oaken framework. The top and bottom bowls were smooth, whilst the middle one was engraved to a depth of $\frac{1}{8}$ inch ; the cloth passed between the top and middle bowls, and was printed by the latter, which received its supply of colour from the bottom one working presumably in a colour box beneath. No mention is made in either patent of copper rollers, of doctors, or of the method of applying pressure to the several bowls, so that it is impossible to say with any certainty what these early machines really were, or whether they embodied the principles upon which Bell subsequently worked in perfecting his own invention. From the depth of the engraving ($\frac{1}{8}$ inch) mentioned in Aitkin's patent, it is fairly safe to assume that his machine was intended for cylindrical block or surface printing, and it is very probable, too, that Keen and Platt's patent related to the same process ; for if an important innovation, such as the continuous printing of calico from the incised lines of a pattern cut on a metal roller, had been introduced by either patentee, it would have attracted too much contemporary attention to have passed unrecorded. In the absence of positive proof to the contrary, then, Bell's claim to priority in the invention of continuous printing from engraved copper rollers cannot well be disallowed. At any rate, whatever uncertainty may exist as to the true origin of the process, it is beyond all doubt that to Bell, and to Bell alone, belongs the credit of having been the first to make a practical success of it.

In its simplest form a printing machine consists of the following parts, arranged as shown in the two diagrammatic sections, figs. 25 and 26 :—

(A) is a hollow copper roller, engraved with the pattern and carried by a steel shaft or mandril (B), which works in bearings on the machine side. It (the roller A) revolves in contact with a cast-iron cylinder or pressure bowl C, above, and with a roller or brush (D)—the furnisher—below, the furnisher (D) being partly immersed in colour contained by a box (E) situated beneath it. A sharp-edged metal blade (F), known as the "cleaning doctor," rests upon and behind the engraved roller, about midway between its points of contact with the bowl (C) and the furnisher (D), and serves to scrape the superfluous colour from the smooth parts of the roller, leaving it only in the lines of the engraving.

At the opposite side of the roller a second or "lint" doctor (G) is frequently placed to catch the loose filaments and nap which detach themselves from the cloth and stick upon the moist surface of the roller. In larger machines which print several colours at a time the lint doctor further performs the useful function of clearing the surface of the roller from the colour that it picks up from those parts of the cloth that have already been printed by other rollers in the pattern. It is easily seen that if these filaments of cotton or the colours from other rollers were allowed to go forward into the colour box, the colour therein would either become unworkable or would be altered in shade, as the case might be. In order to impart to the cylinder (C) the elasticity that is necessary to obtain a full impression of the pattern, it is wrapped with several thicknesses of a special fabric known as lapping (H); an endless woollen blanket (I) also circulates round the pressure bowl, giving additional spring to the surface against which the engraved roller works. The back grey (O) is simply interposed between the blanket and the cloth to be printed (K), for the purpose of preventing the former from being soiled by the colour which penetrates through the latter.

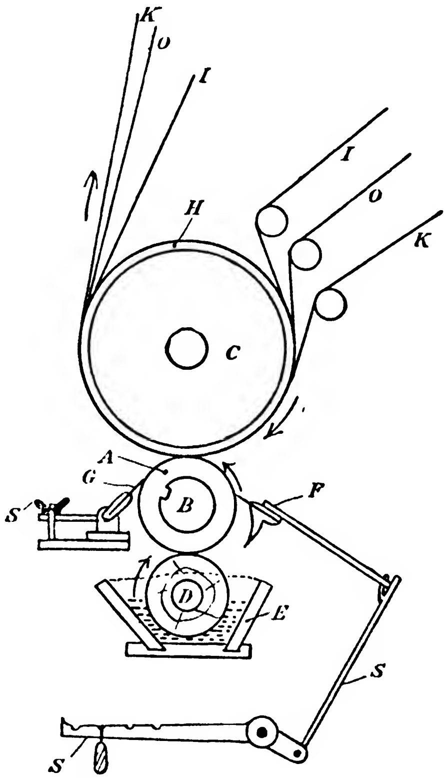


FIG. 25.—Diagrammatic section of a single-colour roller machine.

The whole machine is worked by one large cogwheel (Z) in fig. 26, which gears into a small pinion (Y) on the end of the mandril (B), and is driven from a steam engine, electric motor, or the main driving-shaft of the machine room. On the other end of the mandril another pinion is fixed gearing into a similar one (X) on the spindle of the furnisher, which, therefore, works in the opposite direction to the roller. When a brush furnisher is used it is frequently made to work in the same direction as the roller by means of a small spur-wheel interposed between the two pinions.

The pressure cylinder (C) is not directly coupled to the drive of the machine, but is turned simply by the friction caused by its pressure upon the revolving

printing roller (A). This pressure is usually obtained, in a single-colour machine, from a system of weighted compound levers, at the end of which the cylinder is mounted in adjustable bearings, carried in massive slotted heads, and capable of being raised or lowered, independently of the levers, by means of screws. In this way dead-weight pressure is avoided, and some allowance made for inequalities such as occur when different sorts of cloth are printed at the same time, or when a seam at a piece-end passes through the machine.

In operation the action of the machine is as follows:—The engraved roller (A), during its revolution in the direction of the arrow (fig. 25), first of all receives a copious charge of colour from the furnisher (D); the excess is then scraped off its surface by the doctor (F), and what colour remains in the lines

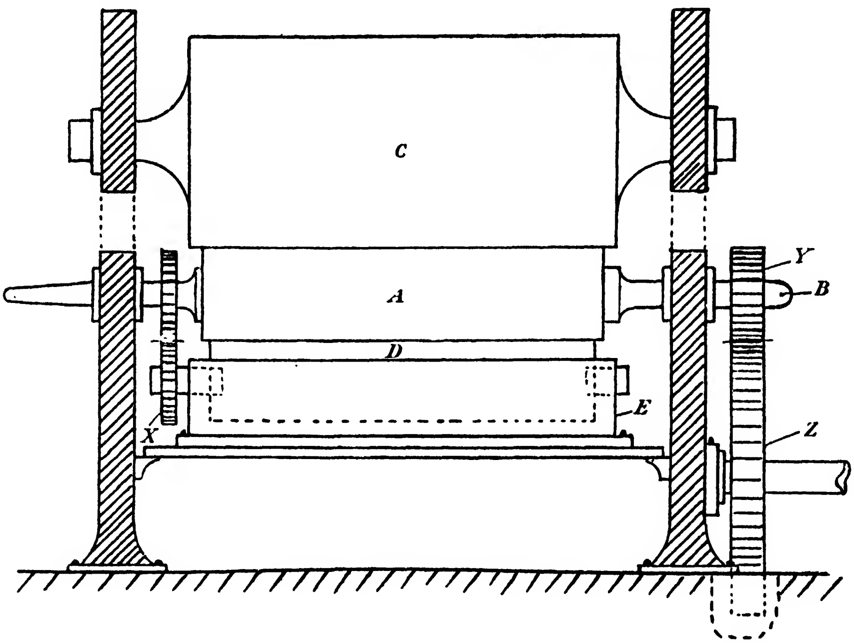
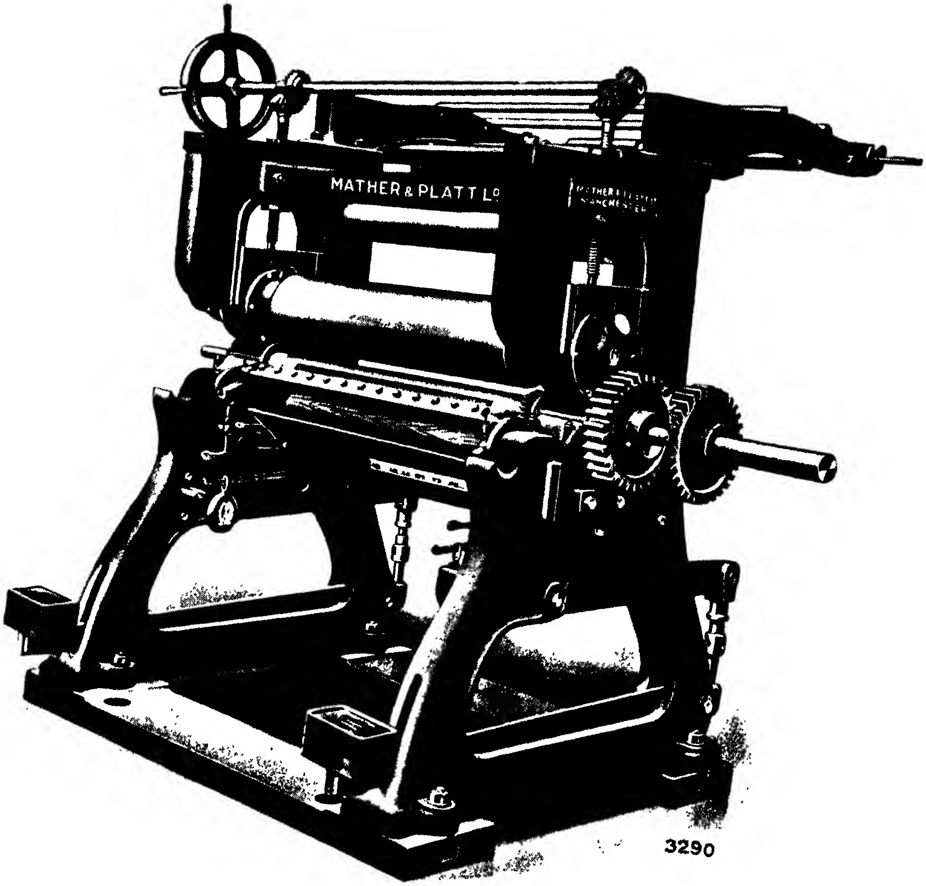


FIG. 26.—Diagrammatic section of a single-colour roller machine. (Doctors not shown.)

of the engraved pattern is then transferred to the cloth (K) to be printed, which, along with the blanket (I) and the " back grey " (O), passes continuously through the machine between the cylinder (C) and the roller (A), and is pressed into and absorbs the colour from the engraved lines of the latter. Continuing its revolution, the roller passes under the lint doctor (G), which clears it of nap, etc., and the same cycle of operations is then repeated again and again without intermission until the whole batch of cloth is printed. After printing, the goods pass directly over steam-heated drying cylinders or " cans," or through a hot-air drying apparatus, or, what amounts to the same thing, between a series of steam-heated iron chests, enclosed in a brick or wooden chamber. When thoroughly dry, they are ready to undergo any subsequent operations that may be necessary to the fixation or development of their colours.

In some patterns of single-colour printing machines, and amongst them the most modern, the arrangements for obtaining pressure between the cylinder and the printing roller are the reverse of those just described, *i.e.* the printing roller is pressed *up* against the cylinder by means of screws and



Single-colour Printing Machine. Blanket and Greys not shown.

[*To face p.* 57.

compound levers which act through sliding bearings in which the roller is mounted (see Plate I.). Where this system is employed it is obvious that the engraved roller and its accessories (the doctors, furnisher, and colour-box) must all move together, and to this end the latter are mounted on plates fixed to the sliding bearings and, in consequence, move along with them.

For the printing of the highest class of shirtings and " plate " patterns, where the engraving on the rollers is very fine, a machine is required of robust and rigid construction with powerful leverage and capable of running at a high speed without overheating. A machine of this description is illustrated in Plate I. The heavy cast-iron framework provides a rigid support for the working parts; it is of strong box-section and is expressly designed to withstand the enormous stresses set up by the great pressure and high speeds incidental to the printing of finely engraved patterns. The cylinder (or bowl) and the mandrel carrying the engraved copper roller, both run in specially designed *roller* bearings, the bearings of the mandrel being so arranged, in spherical housings, that they adjust themselves automatically to any movement or deflection of the mandrel itself. The bearings are easily accessible and the mandrel may be removed or changed without disturbing them in any way; they are packed with grease and additional lubrication may be applied as required through the medium of grease caps. The special steel of which the mandrels are made is subjected to a scientific heat treatment which considerably increases its strength and renders it much more resistant to mechanical fatigue than is the case with ordinary steels.

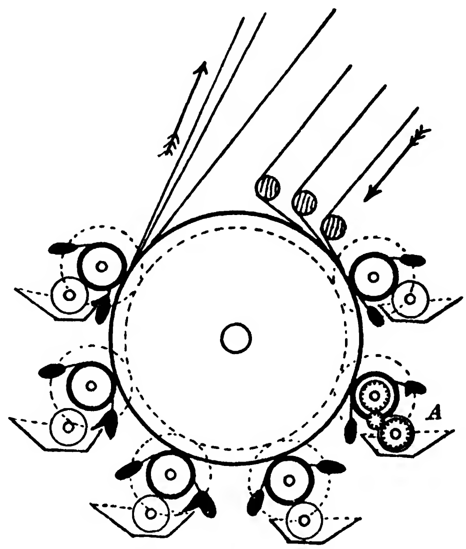


FIG. 27.—Diagrammatic section of a six-colour roller machine.

The dotted circles represent the large "crown wheel" and the six "box-wheels" by which the rollers are driven. At A is shown the arrangement for driving the back furnishers in the same direction as the rollers.

The efficiency of these special features in reducing friction is such that the power required to drive the machine is 40 per cent. less than that required to drive an ordinary single-colour printing machine with plain brass bearings. Moreover, they allow of the machine being run satisfactorily at the high printing speed of 120 to 130 yards of cloth per minute—a great advantage, since it is a well-known fact that the higher the speed of printing the smarter the impression of the engraving.

The construction of machines that are intended to print several colours simultaneously is, of course, more complex than that of a single-colour machine, but such machines may be considered as combinations of two or more single-colour machines, from which they differ in detail rather than in principle. A separate roller is required for each distinct colour in the design, so that a six-colour machine, therefore, has six rollers, each provided with its own colour box, furnisher, and doctors. These rollers are arranged, as shown in fig. 27, round a central pressure bowl or cylinder common to all, and are driven by a single large cog-wheel—the crown-wheel—situated at the side of the machine, and itself driven by any suitable means.

The lapping, blanket, back greys, and cloth are all disposed and pass through the machine in exactly the same way as for single-colour printing.

Each roller of a multicolour pattern is engraved with a portion of the design corresponding to one particular colour; and for the purpose of enabling the printer to fit these separate designs in exactly their proper places on the cloth (and to keep them in register once they are fitted), each roller works in combined spring and lever adjustable bearings, which allow of it being moved whilst the machine is in motion, either (*a*) from side to side horizontally, or (*b*) up and down at either end in a direction tangential to the central cylinder. This latter movement is only applicable within comparatively narrow limits; and although it may sometimes be employed to raise or lower the rollers equally at both ends, its chief use is to preserve their parallelism to each other; for it is obvious that if they were moved too much in this way, their pressure against the cylinder would be appreciably diminished, with the result that an imperfect, or at least uneven, impression would be obtained. If, when all the rollers are perfectly parallel, any one of them happens to print its part of the pattern above or below its proper place *across the full width of the cloth*, it is adjusted, not by being raised or lowered bodily in its bearings, but by having the speed at which it revolves momentarily increased or reduced as the case may require --an effect which is equivalent to raising or lowering the roller without the disadvantage of altering its pressure against the cylinder. This elegant and essential rotary adjustment is accomplished by means of ingeniously contrived differential pinions--known as "box-wheels"--one of which is fixed on the mandrel of each roller, and not only serves to gear it with the main driving-wheel of the machine, but at the same time permits of its speed being regulated, as stated, independently of the driving-wheel, and without interfering in any way with the speed of the other rollers. The following account will convey an idea of its construction and mode of action. It consists of two main parts (see figs. 28): (1) the outer shell (*a*, *a*) carrying the cogs (which go all round in this case and in the driving-wheel, a few only being shown here) and the two projecting lugs (*g*, *g*); and (2) the inner movable disc (*b*) (shown in section, fig. 28A), provided with a hollow axle or sleeve (*c*), slotted endwise as at *f*, *f*, and with the connecting-piece (*d*) through which the adjusting-screw (*e*) passes. The shell (*a*, *a*) is usually about 10 inches in diameter, and 3 inches broad across the cogs; one side of it is hollowed out for the reception of the disc (*b*), which should fit into it as tightly as is consistent with its freedom of movement when turned by the screw (*e*). The sleeve and connecting-piece of the disc (*b*) project through a suitably shaped opening cut through the centre, and between the two lugs (*g*, *g*) of the outer shell. A large-headed screw (N) passes through and slides freely in the slot (*h*) of the outer shell, and is screwed into the disc (*b*) just sufficiently tightly to hold these two parts of the box-wheel closely together without impeding the movement of the latter. In use the box-wheel, after being pushed on the mandrel as far as it will go, is firmly secured to it by driving a cotter through the slots (*f*, *f*) of the sleeve, and through a corresponding cotter hole in the mandrel itself. On screwing up the roller into contact with the cylinder, the cogs of the box-wheel gear with those of the crown-wheel, *i.e.* the driving-wheel. When thus in gear the box-wheel *as a whole* can only revolve when the crown-wheel is revolving; but, by means of the screw (*e*), its *inner disc*, and consequently the roller and mandrel, to which this disc is directly keyed, may be turned round quite independently of either its *outer shell* or of the driving-wheel of the machine. The effect of turning the screw (*e*) is to cause it to press against one or other of the two lugs (*g*, *g*), between which it is confined, and in so doing to move round the inner disc by forcing its connecting-piece (*d*) towards the opposite lug. For example, if, whilst the machine is running, and

the rollers are revolving in the direction of the arrow in fig. 28, the screw be turned towards the circumference of the box-wheel, it is evident that the corre-

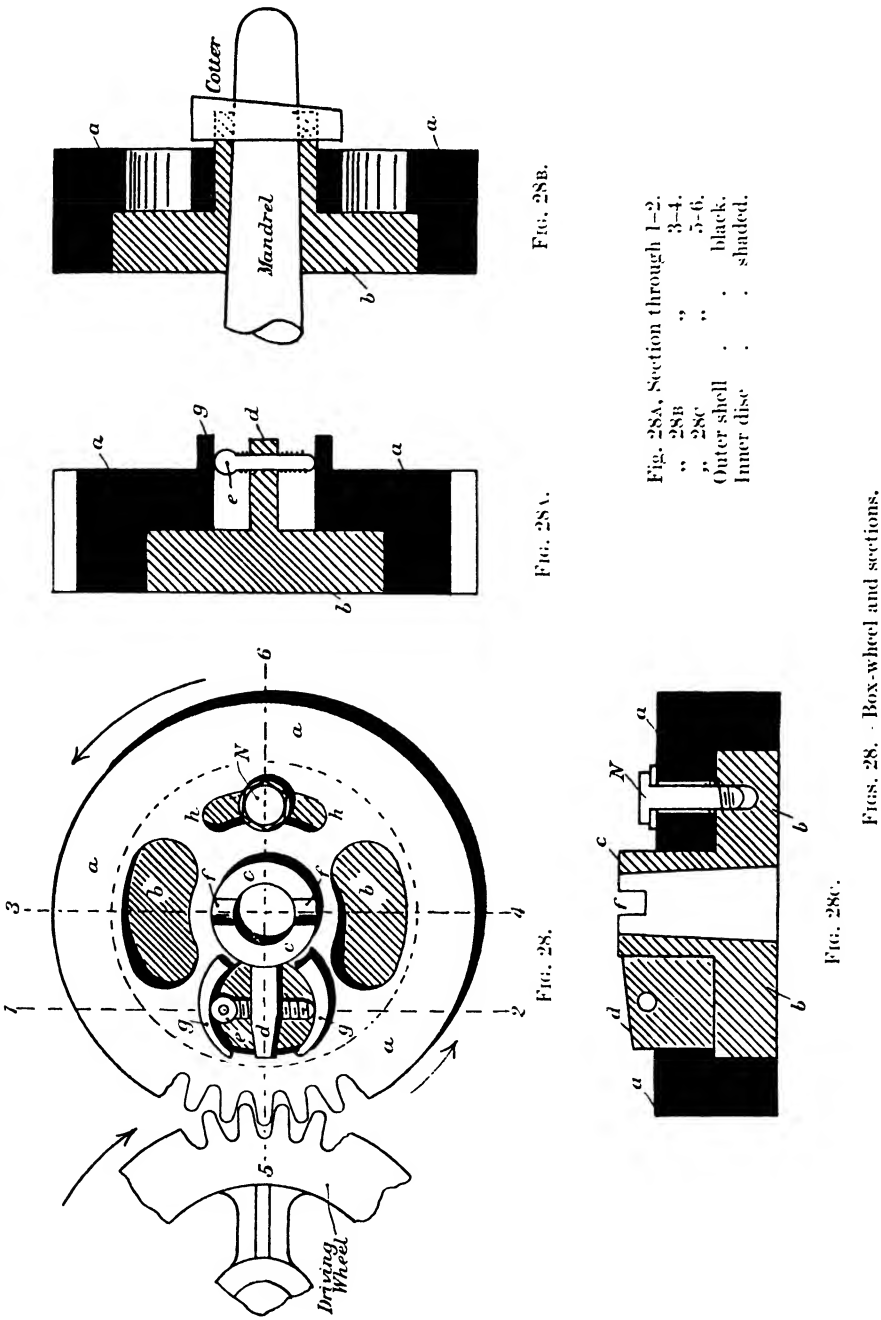


Fig. 28B.

Fig. 28A.

Fig. 28.

Fig. 28C.

Fig. 28A, Section through 1–2.
" 28B " 3–4.
" 28C " 5–6.
Outer shell . . black.
Inner disc . . shaded.

Figs. 28. Box-wheel and sections.

sponding roller will be turned in a direction contrary to its revolution, that its speed will be reduced thereby, and that in consequence its position in relation

to the other rollers will be altered, and hence its impression will appear lower down on the cloth as it emerges from the machine in front of the printer. If turned in the opposite direction, the speed of the roller is momentarily increased, and its impression is raised accordingly. The increase or decrease in the speed of the roller only lasts during the time that the actual turning movement of the screw (*e*) is in progress; after that, it immediately returns to its original speed, but its altered position is permanent, or at least as permanent as the slight unavoidable irregularities in the working of the machine will allow. In this way the impression made on the cloth, by any roller of a multicolour pattern, may be raised or lowered about two inches, whilst the machine is either in motion or stationary, and without affecting in the slightest degree the relative positions of the other impressions to each other. When the ordinary type of box-wheel, as here described, is employed, it will be seen that the rollers must be placed in the machine within approximately two inches or less of their correct positions: but later improvements render this precaution unnecessary, as the most recent box-wheels allow of their inner discs (to which the rollers are attached) being turned completely round whilst their outer shells are still in gear with the driving- or crown-wheel of the machine.

The facilities for horizontal, vertical, and rotary adjustments afforded by the bearings and box-wheels give the machine printer complete control over the movements of his rollers, and enable him to fit together the various component parts of even the most delicate and intricate designs with an ease, accuracy, and despatch impossible of attainment in any other process.

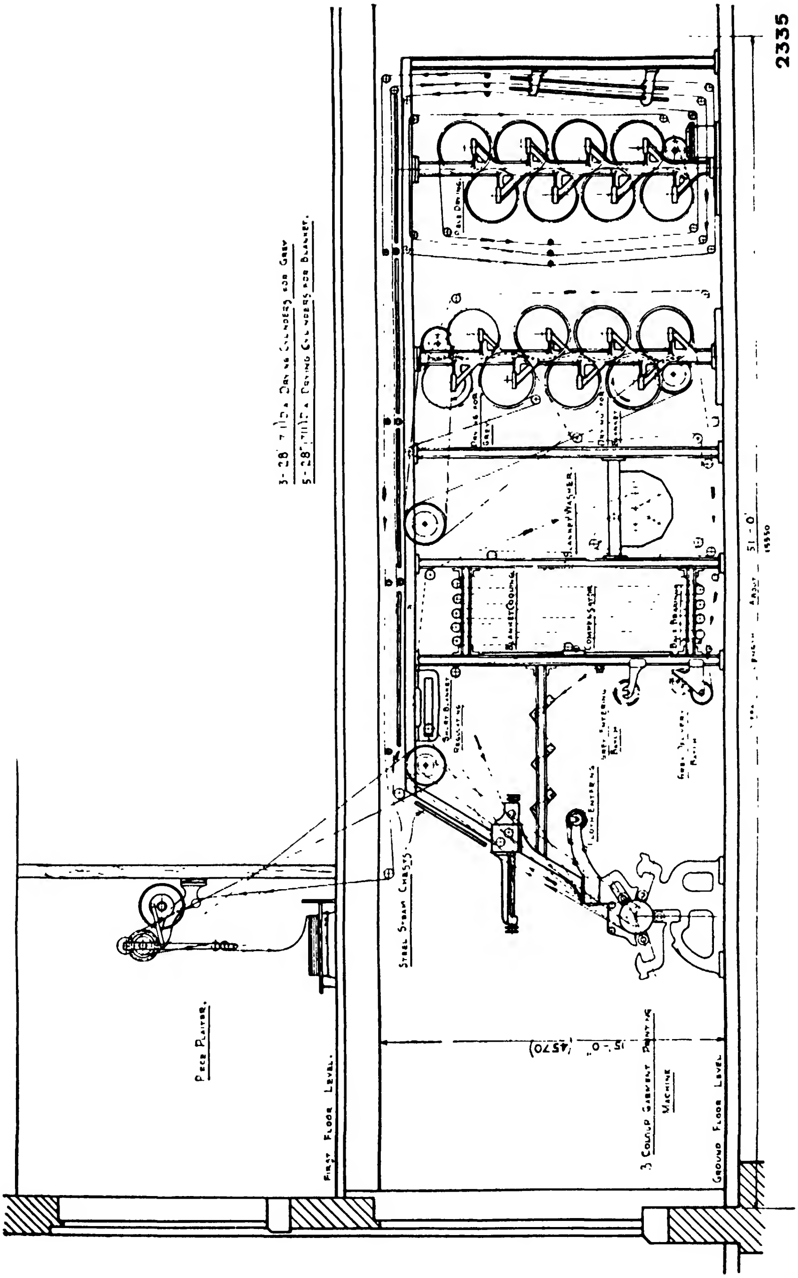
Apart from the extra attention demanded by the increased number of rollers and their accessories, the working of a multicolour printing machine is in all respects similar to that of a single-colour machine. The cloth enters from behind in just the same way, and, in passing between the rollers and the cylinder, receives from each roller in turn a coloured impression of the particular part of the design engraved upon it, so that as it leaves the machine it is found to be fully printed in as many colours as there are rollers.

In Plate II. a sectional sketch of a three-colour machine is shown with Mather and Platt's steam chest and cylinder drying arrangement; and in Plate III. an elevation of a fourteen-colour machine, which shows in a clear manner the disposition of the various rollers and the way in which the traverse motion of the doctors is obtained.

The fitting of the rollers in their proper places is but one part of the printer's work; in addition he has to see that the colour boxes are kept well supplied with clean colour, the back greys and cloth free from creases, and that the doctors, lapping, blanket, and drying arrangements are in the condition best suited to the class of work in hand.

"Doctors."—The management of these apparently simple blades of metal makes, perhaps, greater demand upon the skill of the printer than any other branch of his work. As previously mentioned, there are two kinds of doctors —the "cleaning doctor" and the "lint doctor." The use of the former is absolutely essential in every case, but the latter may be dispensed with or not, at the discretion of the printer.

Cleaning Doctor blades are made of the best quality of medium-tempered steel. They vary in width from 2–3 inches, in thickness from $\frac{1}{32}$ to $\frac{1}{16}$ of an inch, and in length according to the length of the roller, being usually some 2 inches longer. Their top or working edges—*i.e.* those which rest on the roller —are filed to a suitable bevel, and then sharpened by hand with an oil-stone to a razor-like keenness; their bottom edges are firmly clamped between two sheaths of brass (or one of brass and one of iron), tightly screwed together, and furnished at each end with (*a*) a supporting pivot, which rests in a bracket



Steam Chest and Cylinder Drying Apparatus.

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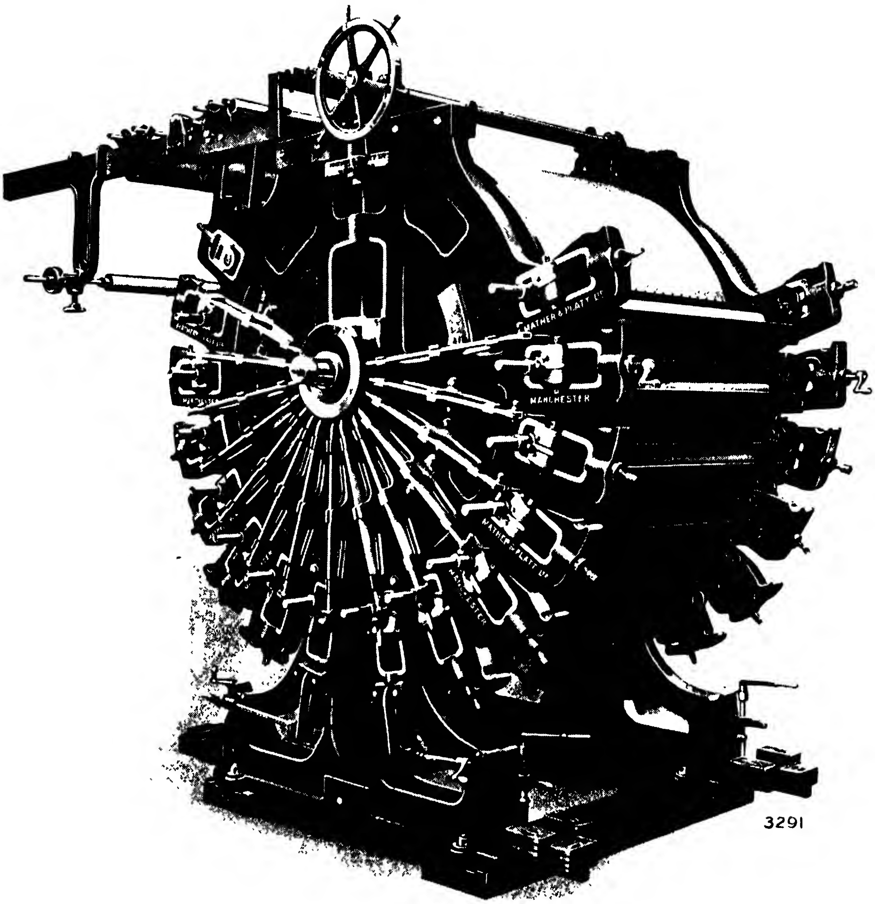

Fourteen-colour Printing Machine.

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attached to the bearing of the roller, and (*b*) a projecting lever, which, by means of weights or screws, serves to press the blade on the roller. The shapes, sizes, and construction of these levers vary according to the place occupied in the machine by their respective rollers—some being simple, some compound—but their general action will be seen by reference to fig. 25, S, S.

In order to prevent the unequal wearing of their edges, which would occur if they were allowed to rest continuously in one position on the roller, cleaning doctors are given a slight to-and-fro movement in a direction parallel to the axis of the roller. This movement is effected by the "traverse motion," which consists of a connecting-rod attached at one of its ends to a pin on the doctor sheaths, and at the other to a small crank or eccentric situated at the side of the machine and worked by bevel gearing. In large machines of modern make the connecting-rod is coupled to an oscillating lever, one end of which works in an undulating channel cut in the circumference of a solid iron disc fixed on the axle of the pressure cylinder and revolving with it (see Plate III.). When this latter arrangement is adopted, the disc is frequently made to slide backwards and forwards on its axle—a device which, by constantly varying the throw of the doctor, adds to its efficiency, especially in the printing of broad stripes, where the width of the engraved pattern is greater than the amplitude of the doctor's to-and-fro motion.

The sharpening or "getting up" of the cleaning doctor edge is possibly the most difficult and most important part of the machine printer's work; for though an apparently simple operation, it demands for its proper performance an amount of skill only to be acquired by long practice, and an unerring judgment as to the kind of edge required for different classes of engraving. No definite rule can be laid down for the production of the edge best suited to a given style of work, for its quality depends not only upon the weight and scale of the engraving, but also upon the thickness and hardness of the doctor blade, the angle at which it rests upon the roller, the pressure applied to it, and upon both the viscosity and tenacity of the printing colour which it has to clean off. Moreover, different printers accord different treatment to their doctors, for even the same class of work, each man preferring to adopt that method which his individual experience has proved to yield, in his hands, the best results. Generally speaking, the edge of a well-got-up cleaning doctor is perfectly straight, absolutely smooth throughout its entire length, bevelled to a rather obtuse angle, and as sharp as a razor; any roughness, unevenness, or the slightest snip in the edge is sufficient to allow colour to escape under it, with the result that the finished print exhibits serious defects in the form of streaks or cloudy patches of colour. Another point which exerts considerable influence upon the efficient working of the doctor, and also upon the durability of its edge, is the angle at which it rests upon the roller; but this, in common with its sharpening, is a matter which only a practical printer can decide, and, in fact, the whole manipulation of the cleaning doctor is so entirely a question of experience and practice that no amount of description could possibly convey an adequate idea of how it varies according to circumstances.

Lint or Composition Doctors only differ from the above in that their blades are made of brass or some similar alloy, and that they have no traverse motion. Formerly, in cases where a colour was affected by the slightest trace of iron, or where it exercised a solvent action on steel, a lint doctor was frequently used in place of and as a cleaning doctor. At the present time it is rarely or never used in this connection, partly on account of its unsuitability for the purpose—its edge being too soft, and requiring to be sharpened up too often—but mainly because the defects which necessitated its being put to such a use have been remedied by modifying the composition of the printing colours.

As regards the getting up of the lint doctor little need be said ; it merely requires to be sharp enough to catch the lint and the colour that the cloth deposits on the roller. It may be noted, however, that a lint doctor ought to press less sharply on the roller than a cleaning doctor, *i.e.* it should occupy a position approaching the tangential rather than the radial. The reason for this is, that as the roller works *towards* (or against) the edge of the lint doctor, the latter, if set at too sharp an angle, is liable to dip into and tear up the engraving—an accident which entirely spoils the roller for the time being, and in many cases entails the turning off of the pattern, and the re-engraving of a quite new roller.

Lapping.—The lapping used for covering the pressure bowls of printing machines is a special fabric, with a linen warp and worsted weft. It is made in various weights to fit it for different styles of work, and upon its quality, both as regards materials and weaving, depends its power of resisting the enormous pressure and the grinding action to which it is subjected during the printing operation. For most purposes eight to twelve thicknesses of lapping are wound round the cylinder or pressure bowl, the utmost care being taken to see that every thickness lies perfectly evenly and is absolutely free from creases. If the lapping is in several pieces, the ends of each must be frayed to a fringe about 2 inches in length, and carefully straightened out quite flat so as to avoid leaving a ridge when the other pieces are wound over them. The slightest crease or any inequality whatever in the lapping is sufficient to spoil hundreds of pieces unless it is discovered at once—not always an easy matter, as many colours do not show up until they are dyed or steamed or otherwise developed after printing. It is of paramount importance, therefore, that the lapping should be properly put on at the outset ; and not only so, but that it should be examined from time to time to see that it is in good working condition. The skill of a printer is displayed as much, perhaps, in the management of his lapping as in the sharpening and manipulation of his doctors. If put on too loosely it very soon slips, and if not re-wound at once, breaks across its whole width, and becomes utterly useless for its special purpose. After working for some little time new lapping stretches to such an extent as to require re-winding ; and all lapping whatsoever requires changing at varying intervals, according to its condition. The longer it is worked, the harder and less elastic it becomes ; and, if the style of pattern for which the cylinder was originally lapped remains unchanged, the lapping itself must be changed, otherwise the quality of the printing will suffer. As a rule, if the lapping is in good condition except in respect of having become too inelastic (from constant use) for heavily engraved patterns, it is not changed at once, but is utilised for the printing of lighter and more delicate designs, the details of which are rendered much better—with a crisper definition, that is—on a fairly hard lapping than on one that is springy enough for bolder work. In this way a good deal of valuable time is saved and the rate of production kept up ; for the changing of lapping is a comparatively slow operation, and whilst it is going on the printer is, of course, producing nothing of saleable value. The quantity of lapping to use for a given style of work and the knowledge as to when it requires changing can only be taught by experience, and on these points the practice of printers varies almost as much as in their treatment of the doctor.

Generally speaking, however, the finer and more delicate the design to be printed the smaller is the amount of lapping required, and the harder or more compact in texture must it be ; whereas for heavy designs, deeply engraved, a larger quantity of a soft, thick, openly woven quality is necessary, especially in cases where the colour is required to penetrate through to the back of the

cloth, or, conversely, in other cases, where the great pressure of the printing rollers against the bowl that it is necessary to employ to obtain a good impression of the pattern on a hard lapping would force all the colours (except the last) of a multicolour pattern too deeply into the body of the cloth, and thus detract from their brilliancy, or "face," as it is technically termed. The durability of any quality of lapping is dependent upon many factors, but, so far as it depends upon the skill of the printer, it is a question of the manner in which it is wound upon the pressure bowl. If it is wound on too loosely, the enormous pressure put upon it in printing causes the several thicknesses to slide about over each other continuously, with the result that the constant grinding action thus set up rapidly wears them away, until eventually the lapping breaks or is torn asunder, and at once becomes utterly useless. As all good work depends, amongst other things, upon the lapping being of uniform elasticity and density throughout, and of a smooth, even, unbroken surface, it is of the utmost importance to guard against these qualities being destroyed by the passage of hard substances between the lapping and the rollers. Even a small nail or other solid body falling into the machine from the floor above, or during repairs, is sufficient to cause a vast amount of damage to both rollers and lapping—damage which frequently entails several hours of skilled labour to repair.

Blankets.—The ordinary printer's blanket consists of from 30 to 50 yards of a thick, pure woollen fabric, tightly woven, and afterwards shrunk and felted. In common with the lapping it must be of uniform texture and of equal thickness and elasticity throughout its whole substance. The function of the blanket is to supplement or increase the effect of the elastic pressure afforded by the lapping, and to this end it is arranged to circulate continuously round the pressure cylinder of the machine between the lapping and the cloth to be printed. In putting it on the machine, therefore, its ends are sewn together so as to convert it into an endless travelling band or web, and sewn in such a way as to leave no ridge at the seam. For this purpose the two ends are first cut perfectly square, then placed in contact with and flush with each other, and sewn together with fine, strong silk thread, the stitch used being generally a sort of herring-bone stitch, which crosses and re-crosses the seam at short intervals, and makes a joint sufficiently strong to resist the working tension of the blanket. When properly sewn in this way a blanket seam ought to leave no evidence on the printed cloth of its passage through the machine; if, however, it is in any way rough or uneven, these defects are at once demonstrated by the appearance of a light-coloured mark right across the whole width of the cloth every time the seam passes. In course of time blankets become hard and soiled from the pressure of the rollers and the wet colour that penetrates through the cloth, and must then either be turned or replaced by a new one. With care and by the use of back greys a good blanket can be made to serve for the printing of 10,000 to 12,000 pieces of calico, and even then be in a condition to withstand washing, after which it may be used again for certain styles of work that make no great demand upon its power of resisting wear and tear.

Mackintosh Blankets.—The mackintosh blanket is composed of three or more layers of fine, evenly woven calico of good quality, cemented together with a solution of india-rubber in naphtha. It is the outcome and the most successful of the many attempts made to replace the expensive woollen blanket by one that would be equally efficient and at the same time much cheaper: and although it is not a quite perfect substitute, it is yet so generally useful that in some works it is employed to the total exclusion of the costlier article. Mackintosh blankets are made in two different forms: one that requires sewing in

the usual way, and the other a seamless blanket, which comes into the market as a single piece of calico, three or four times the required length of the blanket, and coated on both sides with a special preparation of india-rubber, neither sticky nor hard, but just sufficiently tacky to cause the several layers of the blanket to adhere firmly to each other, without any chance of slipping, when pressed together tightly in the printing machine.

To describe in detail the way of putting this seamless blanket on the machine would be useless without a practical demonstration.

One great advantage of mackintosh blankets over those made of wool or cotton is that they can be used with safety for the printing of certain important modern styles in which the employment of strongly alkaline colours is imperative. Such colours, of course, rapidly destroy the wool fibre, and, in the case of cotton blankets, although they do not destroy the fibre, they produce a shrinking effect which renders the blanket less generally useful. A further advantage, too, of mackintosh or other waterproofed blankets is that they can be washed *in situ* and whilst the printing machine is running—a convenience which has led to the introduction of special washing apparatus in which the blanket is cleansed of superfluous colour as it travels continuously through the machine.

Mackintosh blankets are eminently adapted to the printing of fine patterns and shallow engraving ; but, although suitable for most other classes of work, they are better discarded in favour of a woollen blanket when heavily engraved patterns are to be printed, and in all cases where a large quantity of colour is intended to penetrate deeply into the fabric.

Washing- or Wash-Blankets.—Of late years the use of wash-blankets has increased enormously, partly owing to improvements in the washing machines themselves, and partly to the fact that cheap, efficient, and serviceable blankets can now be obtained to withstand the extra strain put upon them. Most of these blankets consist of a single thickness of stout cotton cloth, waterproofed in various ways, and, curious though it may appear, they last better than a 3–4 ply mackintosh. For some styles it is even possible to do good work on a simple grey that has merely been passed through a solution of wax and dried, but, as a rule, a much stronger fabric is necessary. In an important Continental works a strongly woven but fine canvas of the best quality is waterproofed by being passed through successive baths of soap and alum, then dried, padded in a solution of blood albumen, and finally steamed and lightly calendered. These blankets yield excellent results, and are found to be as durable as any of their kind. In many cases the quality of the blanket is much improved by mercerising followed by the foregoing treatment, or by any of the many methods in general use for the preparation of wash-blankets.

Numerous types of blanket-washing machines are on the market. For the most part they are based upon some application of the same fundamental principle, *i.e.* that of subjecting the travelling blanket to the scrubbing action of revolving brushes in conjunction with a copious supply of water.

In some systems the blankets pass between a central drum and a series of revolving brushes arranged at intervals round its circumference ; in others the brushes work against an upright slab or table of slate over which the blanket is drawn ; and in yet others, again, the blanket, carried on guide rollers, simply impinges upon the brushes. With a view to more effective cleansing the revolving brushes are frequently given a to-and-fro or traverse motion across the width of the blanket. In all cases " spirt " pipes are used to throw jets of water at a fairly high pressure on the blanket, and the excess of water is then removed by a doctor, or by a pair of squeezer bowls between

which the blanket passes on its way to the drying apparatus, whence it re-enters the printing machine.

Fig. 29 illustrates one type of central drum blanket washer.

Experience of many of the older types of blanket washer has shown that nearly all possess one defect in common, viz. that they fail to cleanse the edges of the blanket as thoroughly as they do the centre, with the result that colour accumulates, and dries hard, on the edges. If this accumulation is allowed to

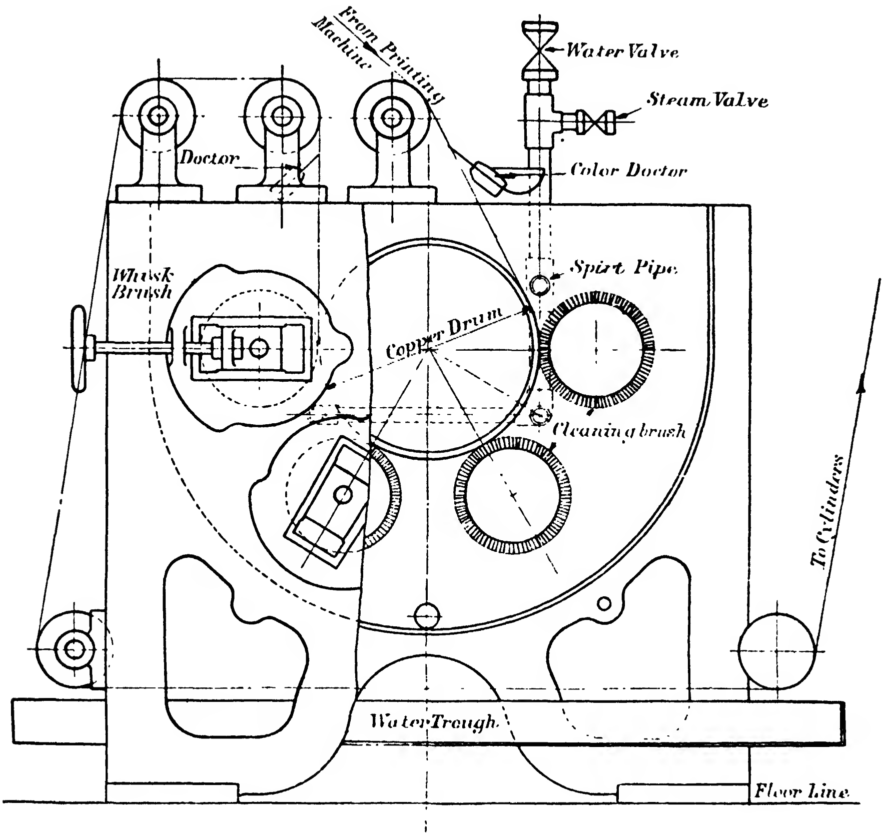


FIG. 29.—Blanket washer (Mather & Platt).

proceed too far it causes the colours on the printed cloth (under which it passes) to " flush " or show a blurred impression. When the machine is stopped, for the purpose of putting in a fresh roll of cloth, the colour from the blanket sticks on the copper printing rollers and, by lifting the doctor, causes streaks and snappers (snaps). These latter defects also arise from the dried colour chipping off in flakes and falling into the colour box, whence, sooner or later, they pass under, and lift, the doctor. Further, as the edges of the blanket become thickened, by the accumulation of colour, the blanket itself begins to run unevenly over the numerous guide rollers, and, little by little, it puckers or wrinkles in the centre (tech. " drives in "), until eventually it appears to be corrugated. If, in this state, it be allowed to pass through the printing machine it becomes either badly creased or actually cut, and in any case it is rendered useless.

The only practicable method of cleaning a wash-blanket from an accumulation of colour is to soak it with warm water and scrape it. For this purpose the washing machine is supplied with hot water, the steam in the drying apparatus is turned off, and the blanket is circulated continuously through the printing machine, it being understood, of course, that only an old roller is in contact with the printing bowl for driving purposes. As the blanket passes upwards in front of the machine the printer scrapes off the softened colour with a steel scraper, and also assists the softening by applying hot water with a stiff brush or a wad of cotton cloth. Cleaning in this way, by hand, entails a considerable loss of time and, accordingly, of production, and its necessity discounts, to a great extent, the value of certain blanket-washing machines in other directions.

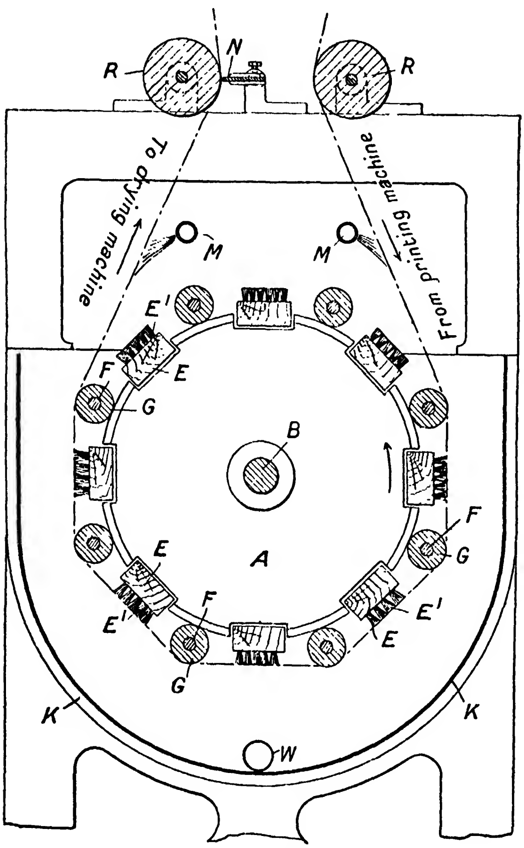


Fig. 30.—Blanket washer (Hindle & Birch).

The desirability of avoiding this expensive operation, and of the other drawbacks incidental to inefficient cleansing of wash-blankets, has long been recognised, and many attempts have been made to overcome the difficulties of the problem. Of these, the most successful, to date, would appear to be the blanket washer patented by T. Hindle and A. E. Birch in 1922.[1]

The principle of this machine is the same as that already noted, but in construction and mode of action the new machine differs very materially from the older types. Reference to fig. 30 will show that it consists essentially of a kind of winch, built up of flat brushes and rollers, around which the blanket travels continuously. All separately revolving brushes and central bearing drums, and all slate or iron tables, are replaced by one single piece of mechanism, the whole machine being of the simplest possible construction.

Fig. 30 represents a transverse section of the machine.

Discs or flanges A are mounted at each end of a central shaft B, and, at intervals, around the periphery, alternating with one another, a series of flat brushes E and a series of guide rollers G are mounted, the adjustment of the rollers being such as to prevent undue pressure of the blanket upon the brushes. The flat brushes and rollers are carried on suitable brackets attached

[1] English patent 188890, 1922.

to the discs at each end of the central driving shaft B, and their length is slightly in excess of the width of the blanket. The shaft B works in bearings in a trough K, K, at the upper part of which the rollers R, R guide the blanket from the printing machine through the washing machine and forward to the drying machine. The blanket is arranged to work with its face, or soiled, side in contact with the brushes, and, as indicated by the arrows, it travels in the opposite direction to that taken by the rotating brushes; and also at a slower speed, the ratio being generally as 2:1. A steel or rubber doctor N removes the excess of water from the blanket as it emerges from the machine, and this and the dirty wash water escape from the surrounding tank or trough K, K through the waste pipe W. The shaft B extends through the side of the tank, and is rotated by a pulley in a direction, as noted above, opposite to that of the travel of the blanket. If desired the flat brushes may be replaced by revolving brushes driven through gearing from the central shaft. So far this modification has not been found to give any increased efficiency.

Where caustic or other colours which destroy the bristles of the brushes are employed for printing, the brushes may be replaced by india-rubber or steel doctors used either alone or in combination.

Many of these blanket-washing machines have been tested, in practice, over a long period and with many styles of printing, and in no instance has a vestige of colour deposit appeared on the edges of the respective blankets, even after months of working. This in itself is sufficient proof of the efficiency of the machine.

In addition, its initial cost is low in comparison with that of other competitors; the cost of upkeep is relatively trifling--the price of the eight flat brushes being less than that of one round brush; it is only a yard wide and occupies very little space behind the printing machine; the brushes never require to be removed for cleaning as they clean themselves by agitating the water inside the blanket; and, finally, the machine consists of only one working part, which is so simply and strongly constructed that it cannot easily get out of order, and, once adjusted, requires little further attention.

The proper preparation of a wash-blanket is as important a factor in its successful working as the cleansing operation. If the blanket is too absorbent the colour cannot be washed out of it; if, on the other hand, it is too heavily waterproofed the colour, pressed through the printed material, lies solely on its surface, and is apt, with deeply engraved patterns, to be crushed or spread out beyond its proper limits. The spread-out colour is transferred to the back of the printed cloth, and by showing through to the face side produces a clumsy impression. In good condition a wash-blanket ought to be just sufficiently porous to absorb the colour it receives, and, at the same time, sufficiently waterproof to prevent that colour from penetrating into the actual fibres of its cotton foundation; in other words, it ought to act similarly to an india-rubber sponge so far as taking up colour is concerned.

The great, indeed the only, advantage of wash-blankets is that, in always presenting a clean, dry surface to the back of cloth, they render the use of back greys or "bumps" unnecessary.

Back Greys.—Back greys, as previously mentioned, are simply pieces of unbleached calico that are run between the blanket and the cloth to be printed, for the purpose of protecting the former from the colour that percolates through the latter. They are always used for woollen blankets and ordinary mackintosh blankets, but may be dispensed with altogether when washing-blankets are employed, though they are sometimes used along with them for certain styles of pattern. After being used as back greys, the cloth is sent into the bleach-croft, and, after "souring" to get rid of the metallic salts and thickening agents

that it contains, is bleached in the ordinary way, and used for printing just like any other cloth. Calico that is destined for madder work is never used for back greys, on account of the fact that in most cases the mordants and other bodies it picks up in process cannot be perfectly removed in the usual course of bleaching, and consequently show up when the cloth is dyed. "Bumps" is a name applied to calico set apart specially for use as back greys, and "bump greys" are always employed, as far as possible, in the printing of colours that are either very difficult to bleach out or that affect the cloth in other irremediable ways—such colours, for instance, as Aniline black, Indigo blue, and the alkaline discharges used for tannin mordanted cloth and Turkey red.

In works where the printing machines are not fitted up with blanket washers the difficulties of the management are increased considerably by the necessity of providing a suitable back grey for every piece of cloth printed. A stock of cloth, greatly in excess of what is actually required for the execution of orders, must always be kept on hand, and must, moreover, be bought with due regard to the width of the cloth along with which it is intended to work; for if the grey be too narrow it is useless, and if too broad it gets daubed with colour on its edges, and not only wastes colour, but dirties every part of the machine with which it comes in contact—rollers, drying apparatus, etc.—and adds to the difficulties of producing clean work. Apart from the capital involved in stocking a large quantity of cloth, the extra time and labour expended upon the handling of back greys augments the cost of production, and their storage takes up a good deal of valuable space. Taken altogether, the question of back greys is one of the most irritating that a works manager has to deal with; and it is not surprising, therefore, that every step taken towards their abolition should meet with the approbation of technical men.

Back greys are usually seamed on a fine sewing-machine, and for ordinary purposes this is quite sufficient, but where very delicate and full all-over patterns, like zephyrs, minute checks, etc., etc., are to be printed, the ends of the greys, instead of being sewn, are pasted together, so as to avoid the least chance of a ridge being formed.

Furnishers and Colour Boxes.—The furnisher is simply a wooden roller (covered with cotton or wool) which revolves on brass centres in slots cut in the ends of the colour box. Below, it dips into the colour, and above, works in contact with the printing roller, to which it furnishes a constant supply of colour. For most styles of work this plain wooden furnisher is sufficient, but for colours containing much solid matter, such as zinc oxide, sulphur, chalk, and pigments like chrome yellow, it is replaced by a stiff revolving brush, which, in addition to supplying the printing roller with colour, serves to scrub out any deposit that may stick in the engraving, and thus prevents the production of weak impressions. In order to render this latter operation more effective, the brush furnisher is frequently made to revolve against the roller, but this is not essential except in the case of strong pigment colours—especially Guignet's green.

The colour boxes are long, narrow, shallow troughs of wood or copper, supported at each end on small shelves or brackets, carried on a cheek of iron attached to the adjustable bearings of the printing rollers, and moving backwards and forwards with them, so that whenever the pressure of the roller against the cylinder is altered, the relative positions of roller, colour box, and furnisher to each other remain the same. Double-cased colour boxes of various types are used in cases where the colour requires to be kept either very cool or worked hot. For cooling purposes ice is packed between the two casings, while for keeping the colour hot, steam is passed continuously between them.

Rollers.—The rollers used in calico printing are of two kinds—solid and shell. Both types vary in length from 32″ to 80″, and also in diameter, the solid rollers being restricted, for several reasons, to the smaller sizes, viz. those between 5″ and 12″ in diameter. On the other hand, shell rollers may be anything from 5″ to 30″ in diameter, though one firm in England is fitted up to print, and has printed, patterns with a vertical repeat of nearly 120″—equal to rollers 40″ diameter. These large sizes are, however, unusual, and very few firms are able to produce patterns exceeding 36″ in vertical repeat.

The ordinary solid roller is approximately 5″ diameter, and long enough to take a pattern 32″ wide ; it consists of a hollow cylinder of copper, the walls of which vary in thickness from $\frac{1}{2}$″ to $1\frac{1}{4}$″ ; its surface is ground perfectly smooth, and its circumference must be exactly the same from end to end. Inside, a "tab" or tongue of metal ($\frac{1}{2}$″ broad and $\frac{1}{4}$″ deep) extends throughout the whole length of the roller. This tab fits into a corresponding slot cut in the shaft or mandrel, upon which the roller is forced when required for printing, and serves to prevent it from slipping round during this operation. Solid rollers are cast, and afterwards hammered or rolled to increase their density, and to ensure that they will yield a smooth, even surface, free from granulation, when turned, ground, and polished.

"Shell" rollers consist of a cast-iron foundation, upon the surface of which a coating of copper is deposited electrically. This coating varies in thickness according to circumstances, and must be deposited slowly and carefully to avoid granulation or porosity, either of which would render it altogether unsuitable for its special purpose. When a sufficiently thick coating of copper is obtained, the roller is taken out of the depositing vat, well washed, put into a lathe, and ground and polished to size. If its surface is at all granular, it is burnished under a heavily weighted, polished agate ; but nowadays the science of electro-plating is so well understood that, in the majority of cases, this final burnishing is unnecessary. The iron foundation or shell is in all respects, except that of material, identical with a solid copper roller, and a shell roller, therefore, may be used for precisely the same purposes as a copper one ; in fact, both types are used in the same pattern in scores of instances.

Solid copper rollers are undoubtedly the best from every point of view, save that of expense ; and even there it is only the initial cost that is greater than that of shell rollers. The great advantage of solid copper rollers is that when the pattern engraved upon them is no longer in request it can be turned off in the lathe and a new one engraved in its place ; and this can be repeated until the roller becomes too thin to use. In addition to this they are much more durable, much less liable to accidents, and much more easily repaired when damaged than are shell rollers. They are also eminently adapted to every style and method of engraving : and if any one of a series of solid rollers, each of which ought to be of exactly the same diameter, is out of size, the mistake can be remedied with the greatest of ease in the lathe. On the other hand, shell rollers are comparatively cheap ; they can be made on the spot ; they are lighter to handle ; and if well made, they are reliable in use, and can be applied to most of the ordinary styles of printing. But unless the deposit of copper is fairly thick, they cannot be turned off and used again for another pattern ; neither can they be so easily and readily repaired, for if they are seriously cut or dented it is most difficult to patch or plug them without lifting the copper in the surrounding parts. And again, if they are dropped, receive a heavy blow, are submitted to unequal pressure, or subjected to the great heat that is sometimes engendered by the friction of the mandrel in the bearing, the coating of copper on their surface is very liable to be loosened from the shell, with the result that the roller becomes absolutely useless until it is

re-coppered and re-engraved. If this loosening of the copper of a shell roller is not detected at the time of its occurrence, it usually manifests itself in no unmistakable way the next time the roller is put into the printing machine; for, immediately the machine gets well under way and heated up a little, the loosening begins to extend, until finally the lint doctor dips into the engraving of the slightly bulging parts and, by tearing the copper bodily away from the shell, spoils at the same moment the lint doctor, the cleaning doctor, the blanket, and the lapping. On the whole, however, shell rollers are exceedingly good substitutes for solid copper ones; and, now that their manufacture is thoroughly understood, they may be used with the utmost confidence for most classes of work, and may also be engraved by machine if the copper is moderately thick and the pattern not too heavy. Perhaps the greatest convenience afforded by shell rollers is that they can be made, with perfect safety, to any size desired.

For instance, at the works of Messrs F. Steiner & Co. Ltd., Church, Lancashire, who possess the largest printing machine in the world, one of the authors has dealt with ten-colour patterns, the shell rollers for which were each 80″ in circumference and 80″ wide, and at the same works some of the rollers employed for "sarries" and imitation "batticks," etc., are even larger. In these huge rollers the copper is deposited upon an iron drum, the hubs of which are bored to fit the ordinary mandrels used in the machine. If made in copper alone they would have to be very thick to overcome their tendency to spring in the middle during the printing operation, and would consequently be enormously expensive; and if thin enough to be of reasonable price, they would be very liable to distortion during the course of the various processes and handlings they go through from the time they are first made to being used for printing. Copper deposited on a rigid hollow iron drum, however, is free from these drawbacks; and although large rollers made in this way are somewhat difficult to manipulate in practice, they yield surprisingly good results when everything is taken into consideration.

Printing rollers are sometimes made of brass, but they offer no advantages over copper rollers, and, if anything, give more trouble, on account of the extra time it takes to burnish out fine scratches, which can be repaired in a few minutes on a copper roller by the printer himself, with a small finger-stone and a steel burnisher. Occasionally, too, copper rollers are nickel-plated to increase their surface hardness, but they are then open to the same objection as brass rollers; and, in addition, the film of nickel is apt to peel off, with disastrous results if it occurs whilst the machine is printing.

During the last few years chromium-plating has been applied successfully to copper printing rollers. Its effect upon the surface hardness and wearing quality of the rollers is so pronounced that even the thinnest film of chromium is sufficient to increase the life of a printing roller forty- or fifty-fold. Comparative trials have shown that whereas an ordinary pad roller requires re-engraving (or "running up") after printing 7,500-12,000 yards of cloth, a similar roller, chromium-plated, will print 480,000 yards and still be in fair condition.

The rollers are engraved before plating, and the film of chromium deposited upon them is so thin that no appreciable alteration in the scale of engraving is noticeable.

Mandrels.—Mandrels are the long steel shafts which serve as temporary axles for the printing rollers when the latter are placed in the printing machine. They are usually about a yard longer than the roller, and project 18″ beyond it at each end. For a distance of 6″ or 8″ on each side of the roller these projecting portions of the mandrel are turned to a perfectly cylindrical neck, so

as to work smoothly in the brass steps of the adjustable bearings in which they turn; for the rest they are tapered off, at a convenient angle, to facilitate the slipping on of the rollers and box-wheels, and to reduce their weight. The middle part of the mandrel (between the necks), upon which the roller is forced, corresponds in diameter to the internal diameter of the roller that is intended for it; it is slotted from end to end for the reception of the "tab" inside the roller, the size of the groove being slightly larger than that of the tab; and it tapers a little, so that the roller may be forced tightly upon it. It ought to have been mentioned before, that the roller itself also tapers *internally* in exactly the same way. The forcing of the rollers on the mandrels is done in a special machine, and requires to be performed with care, as, if the full power of the machine is exerted too suddenly, both roller and mandrel are

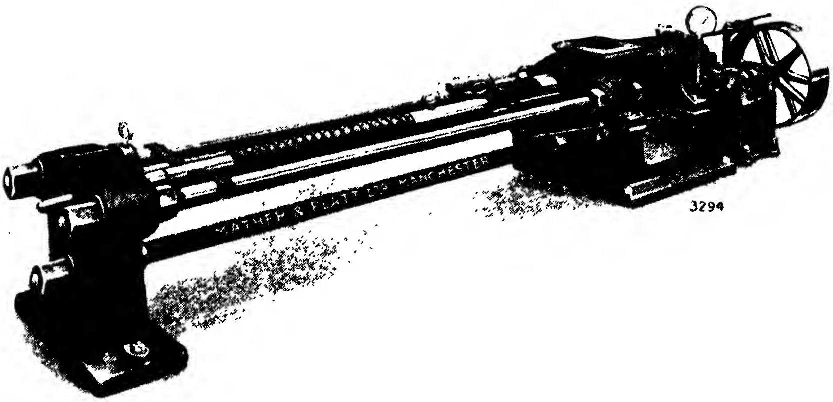


FIG. 31.—Hydraulic forcing machine for rollers.

liable to be strained and rendered quite useless for the time being. Fig. 31 shows a forcing machine or "jack" for copper rollers.

ENGRAVING OF COPPER ROLLERS.

The engraving of printing rollers is a distinct and a highly specialised branch of calico printing, and has been developed, in various directions, to such an extent that at the present time it may be looked upon as a separate industry. So much so is this the case, that many firms devote themselves exclusively to the engraving of copper rollers; and it is not at all uncommon for small calico printing establishments to depend entirely upon such firms for the engraving of all their patterns. Larger concerns, too, send a great many of their most important designs to be engraved by outsiders sometimes because their own engraving department is too small to cope with all the work they require, sometimes because their staff is not sufficiently expert to execute the best class of engraving, and sometimes in order to relieve themselves of the responsibility for difficult work, and thus ensure themselves against loss; for, of course, if the engraving cannot be made to give a satisfactory rendering of the original design, or the delivery of the rollers is a long time overdue, they have a claim against the engraver. From this it will be seen that a practical calico printer is not necessarily a practical engraver as well; at the same time a knowledge of the different methods of engraving is vastly interesting, and, to a certain extent, most requisite to enable the calico printer to recognise

more fully the scope of his art. To this end, therefore, the following remarks will be confined, the more so as the limits of the present work render impossible anything more than a brief explanation of the three principal methods of engraving. Even these methods embrace so many different processes, and call for the application of machinery of such complexity, precision, and delicacy, that justice could only be done to them in a treatise devoted specially to the subject. Compression is necessary; and consequently, while referring the reader to larger works, such as E. Berthoud's *Traité de la gravure sur rouleaux* and *Engraving for Calico Printing* (Blackwood), for details respecting the methods of practice and the machines employed in engraving a design on copper rollers, a brief résumé of the following is all that can be given here—Hand engraving, Machine engraving, and Pantograph engraving.

At the outset it may be well to note that the object of each method of engraving is the same, and that the results of each, although achieved by very different means, present the same general appearances. Lines are obtained by the cutting of a simple furrow or groove in the roller; solid objects, by first engraving the outline, and then filling in the space thus enclosed with parallel lines, engraved close together so as to form a series of angular corrugations, something like the surface of a file. The number of these corrugations or lines to the inch constitutes what is known as the "scale" of the engraving, and the coarser the scale, the deeper must be the engraving, and the more colour will the roller put on the cloth. As several scales can be engraved on different parts of the same roller, it follows that, from a single roller, several tints of one colour can be printed at one operation. In theory it is possible to obtain every gradation of colour tone between pure black and pure white from one engraved roller; but in practice it is found that the uneven surface of woven fabrics is incapable of receiving the impression of more than two or three of the numerous gradations that may be engraved on one roller, and consequently it is but rarely that more than three shades or gradations are attempted on a single roller, any additional shades that may be required being ordinarily obtained from a second or even a third roller. A shaded effect may be obtained from a *single* roller, especially if it be engraved in stipple, but such work is usually unsatisfactory on account of its "speckly," "pinny," or patchy appearance. To avoid this defect, a second roller is engraved to print a flat tint *over* the whole of the shaded work on the first, the effect of the two wet colours falling together being to cause the shaded portions, which are printed in a dark colour, to swell or run into the pale superposed tint, with the result that each tone blends with or melts into its neighbours in a perfectly imperceptible manner. It is not necessary even to print a pale tint of the colour used for the shaded roller; a colourless paste will do quite as well so long as the moisture required to cause the swelling is applied to the cloth, or an entirely different colour may be employed, in which case the double gradation of tone and colour is obtained. For instance, if the shaded part of the pattern is printed in red with a yellow superposed, the effect obtained will not only show gradation of tone, but will also display an exactly corresponding gradation of colour, ranging from dark red, through various shades of scarlet and orange, to pure yellow. This facility for the production of various effects from few rollers is one of the most important qualities of roller printing, and one that is largely utilised in every printworks.

As a rule, a combination of line and stipple is employed for engraving gradated effects on copper rollers; very light line engraving is not suitable for the most delicate tones, and heavy stipple engraving cannot be made to give an even shade over an extended space of solid colour. But using the two styles together, very good effects are easily possible. For example, in expressing

the idea of a flower in light and shade, the darker parts of it and those in shadow would be engraved in line, to print as solid patches of colour ; from these, lines of diminishing thickness would be made to radiate, according to the shape of the petals, and finally dots (or stipple) of various sizes and depths, and at constantly increasing distances from each other, would be added between and beyond the radiating lines, to complete the scheme of gradation. Rollers engraved in this way, when printed in conjunction with superposed colours, yield wonderfully delicate effects of shading, but it is questionable whether the amount of work they represent is justified by the effect obtained ; artistically speaking, flat effects based on frankly conventional lines, with gradation suggested rather than realised, and unmarred by fussy detail, generally give more satisfaction to those best able to appreciate the highest class of decorative work ; but, at the same time, stippling is quite an easy and natural process in metal engraving, and if used with restraint, it is difficult to see what objection there is to its employment.

Fig. 32 illustrates the usual treatment of a roller engraved to give effects of shading ; the dots are exaggerated somewhat for the sake of clearness.

Another method of producing effects of light and shade is to engrave the entire design in various shapes and sizes of delicate masses and different qualities of graduated line, the whole surrounded by a fine regular outline, and then printed in a dark, rich colour. This style is usually employed for single-colour effects, but its range may be extended by allowing a second roller to print a pale flat tint over the greater part of the pattern, the unprinted portions of the cloth then showing in white as high lights.

FIG. 32.—Example of stipple engraving.

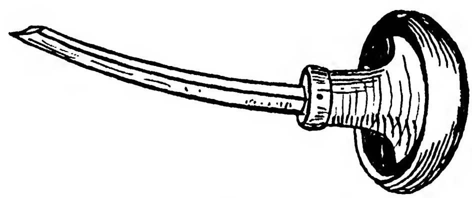


FIG. 33.—Burin or graver.

Numerous other effects of line and stipple, solid mass and superposition of colour, are also in general use ; in the possible combinations of the various qualities of copper roller engraving almost any effect capable of being printed can be obtained, and nowadays it is not so much a question as to how a certain effect is to be got as it is of the *cheapest* way of getting it.

Hand Engraving.—The principal implements used in hand engraving consist of gravers or burins, small punches and light hammers. The gravers are made of fine quality steel bar, square or rhomboidal in section, slightly tapering from handle to point, curved a little, so as to enable them to be worked almost parallel with the roller, and mounted in a short wooden handle with a rounded end. Their points are obtained by grinding the ends off at an angle, so that their cutting edges are formed by the edges at the outside of the curve (see fig. 33).

In use, the graver is held between the thumb and forefinger, and the handle in the palm of the hand. The point is guided by the thumb and driven forward by the pressure of the palm, the tool being held at an angle very slightly

inclined to the roller. The pattern to be engraved is transferred to the roller by any suitable means—generally from a tracing in lampblack and oil, or in some colour containing a soluble sulphide, which, when laid upon the surface of a moist roller, leaves its impression in black lines of copper sulphide. After the pattern is engraved, the roller must be polished with "Water of Ayr" stone and water, to remove the burr raised by the action of the graver; and after that it must be burnished, if required to print very intense colours, since the fine scratches left on its smooth surface after stoning tend to leave their impression on the cloth (tech. "scum").

Roller-engraving by hand is a slow process. It is only used for the most delicate and important work, and for large designs of which only one repeat can be put on the roller, and which are therefore too big to be engraved by any other method.

Stippling is a form of engraving that, until recently, was only possible of execution by hand. In principle it is simple enough, being merely the punching of small dots on the surface of the roller, but in practice it is most difficult to do well, as it requires the utmost delicacy of hand in its final stages. The slightest inequality or suddenness in gradation tells at once in the printing machine; and if the defect is caused by the stipple being too deep or strong, it means that it must be burnished or polished down and re-engraved—an operation which affects the neighbouring portions of the engraving, and thus makes it necessary to re-touch a good deal of the work that was previously satisfactory. Stippling is performed by means of fine, sharp-pointed steel punches, which are held in position on the roller with the left hand, and then lightly tapped with a small steel hammer held in the right hand. The dots are afterwards deepened by drilling. The handle of the hammer is from 8 to 9 inches in length, and made of a springy wood, which ensures the rebounding of the head from the top of the punch, and so adds to the delicacy of the engraver's touch. The difficulty of stipple engraving will be better understood when it is remembered that every dot engraved raises a minute burr, higher in proportion as the dot is deeper, and that consequently the engraver has to make due allowance, at every stage of his work, for the final polishing off of the surface roughness caused by the thousands of burrs thus produced, which if allowed to remain would lift the doctor blade every time they passed under it in printing, and give rise to faulty work.

Stippling is no longer a monopoly of the hand-engraver. So far as calico printing designs are concerned, the stippled parts can now be much more economically and quickly engraved by mechanical means. The results obtained are more perfect in execution, and the final effects are as satisfactory as those produced by hand work. A short description of the processes employed will be found under pantograph engraving.

Machine Engraving.—In machine engraving the pattern, instead of being cut clean out of the surface of the roller with a sharp instrument, is stamped or indented thereon by means of a previously prepared mill with the design raised upon it in *relief*. The making of this mill involves many consecutive operations, and a number of details to which the most careful attention must be paid to ensure success.

In outline the process of machine engraving is as follows:—At the outset, if the pattern has not been designed for a definite size of roller, it must be altered in scale to repeat exactly a given number of times around the circumference of the roller upon which it is to be engraved. One repeat of it is then transferred to, and engraved by hand upon, a small roller of softened steel, known as the "die." Formerly the transfer was made from a tracing in printer's ink or a similar composition, but at the present time it is frequently carried out in

the following manner, which has the advantage of giving a non-smearable transfer.

The polished and perfectly clean plain die is immersed in a solution of copper sulphate until its surface is evenly coated with a deposit of metallic copper; it is then washed, dried, and has wrapped round it a tracing of the pattern executed in a colour containing a sulphide; the tracing must be wrapped so that the repeats join up exactly, and in order to prevent it slipping it is made on a polished or varnished paper, which, when slightly damped by being breathed upon, adheres firmly to the die; the whole is now wrapped tightly in several folds of stout paper and tied round with string, being allowed to stand an hour or two, after which, when the coverings are removed, the pattern is found to be transferred to the die in lines of copper sulphide. The engraving of the die completed, the next process is that of hardening. For this purpose the die is first painted with a thick coating of a chalky composition, to prevent its surface from oxidising, then packed in an iron case containing bone-ash, and sometimes a little charcoal, and heated to a cherry-red heat in a special furnace, after which it is plunged into cold water, and finally tempered to the requisite hardness. It ought to have been noted that, before hardening, the surface of the die outside the limits of the pattern is punched all round with fairly deep indentations, the object of which is to raise a coarse burr at each side of it—a burr which prevents lateral movement during the subsequent operation of "clamming." To make the mill, the die, engraved and tempered as above, is now placed in a specially constructed rotary press—the "clamming machine"—and screwed by hand into close contact with another small roller similar to itself, but of *softened* steel—the mill. The machine is then set in motion, and the first effect of its action is to cause the burrs on the indented edge of the hardened die to sink into the softer metal of the mill, and gradually, as the pressure is increased, to force this latter into the indentations themselves, thus raising corresponding projections on the mill, some of which, being always in mesh, or gear, so to speak, with the die, effectually prevent the two from slipping backwards and forwards laterally during their rotation. The die and mill are then kept revolving in frictional contact with each other, and under constantly and regularly increased pressure, until the soft mill has taken an impression in *relief* of every line and stippled dot engraved on the die. During this operation the mill and die must be daubed freely with lubricating grease, and it is, moreover, especially important to apply just the right amount of pressure, as otherwise the work will be defective. If the pressure is too light, the pattern will be incompletely transferred to the mill; if it is too heavy, the mill is liable to be crushed out of shape, the relief to be damaged, and the die either strained or broken. After clamming the mill is placed in a lathe and has its rough edges turned off and tapered to below the level of the background of the relief, so as to prevent any part of it except that carrying the pattern from coming into contact with the copper roller during the process of engraving It is now hardened in exactly the same way as the die, and, after cleaning, it is ready for use. The dimensions of dies and mills vary according to the style and scale of the patterns to be engraved. As a general rule, however, the circumference and the width of the working surface of a die correspond to the vertical and side repeats of the design; but in the case of very small "all-over" cover patterns, which really repeat at very short distances, several repeats are necessarily put on a single die. The dies usually employed vary between ½″ to 6″ in length, and 3″ to 9″ in circumference. As regards the size of mills, they may be any multiple of the die in circumference so long as they will repeat a whole number of times round the copper roller; in length or width they must, of course, correspond with the die.

The machine used for engraving the full-sized roller from a small mill is too complicated to describe in detail here, and for particulars of its construction and working the reader must consult one of the treatises dealing specially with the subject of engraving. Briefly described, however, it consists of two strong cast-iron ends, connected together with long wrought-iron stays and each provided with a bearing in which a shaft or axle revolves. This shaft, upon which the roller to be engraved is fixed, may be turned either by hand or power, according as to whether its movement is to be continuous or intermittent. At the back of the machine, and a little below the level of the shaft, a slide or rest extends from end to end of the machine. Along this rest a strong pillar-like support for a hinged lever is arranged to travel to and fro when actuated by means of a screw fixed between the double bar of which the rest consists. The long lever, hinged at one end to the top of the travelling or adjustable support, extends forward to the front of the machine at some distance above the shaft (and roller), and is furnished at a point immediately over the axis of the latter with an adjustable block-bearing for the reception of the mill, which thus rests exactly on the top of the roller when the machine is in use. In addition to these essential parts, a modern engraving machine is provided with various other fittings and devices, designed with a view to giving the engraver perfect control over every movement, and to enable him to adapt it to different sizes of rollers and to special styles of engraving.

The actual engraving is performed as follows:—The roller is first securely fixed on the shaft, and then the mill is brought to bear upon it at one end, the utmost care being taken to see that the two are perfectly parallel, and that their respective axes are in perfect vertical alignment with each other. Any deviation from these conditions results (*a*) in misfitting of the repeats, and (*b*) in more or less loss of crisp definition, especially in strongly engraved patterns. The machine is now set in motion, and as the roller is in frictional contact with the mill, the two revolve simultaneously, and the latter indents its pattern into the surface of the former. At the commencement of the engraving the pressure of the mill upon the roller is comparatively slight, but, after the first circuit of the roller is completed in shallow intaglio, it is gradually increased from time to time by adding weights to the free end of the lever, until the pattern is engraved as deeply as may be. When a part of the roller equal in width to the length of the mill is fully engraved all round, the mill is lifted, and, together with the pressure lever, is moved laterally to its next position by means of the travelling lever-support. The next position is, of course, that in which the side repeats join up exactly to complete the pattern. The operations are then repeated again and again until the whole roller is fully engraved. It is then taken out of the machine and polished as usual.

In fig. 34 (which pretends to no more than illustrate, in simple diagrammatic form, the principle of machine engraving) the disposition of the essential parts of an engraving machine is shown. R is the roller, M the mill, B the adjustable bearing for the mill, L the pressure lever, X the slide rail or rest, S the sliding support carrying the lever, W the weights for applying the necessary pressure to the mill, and Z the screw or worm for altering the lateral position of the mill.

The introduction of machine engraving not only cheapened and accelerated the process of engraving, but at once rendered available many styles of design that were previously either impossible or too expensive to engrave by hand. Such, for instance, are small cover patterns and fine fancy stripes which repeat hundreds of times on an ordinary sized roller, and which would occupy a skilled engraver many weeks to execute by hand. If executed by machine, however, one single repeat or a solitary stripe of such patterns, engraved on

a die, would be all the hand-work required for the engraving of a full-sized printing roller, and the work would not only be done more expeditiously and cheaply, but would be much more regular than if engraved by hand.

As the dies of a pattern are always preserved it is obvious that, in addition to increased speed of production and economy of skilled labour, machine engraving also affords special facilities for the rapid re-engraving or strengthening of a roller that is worn down, or for the replacing of a broken or worn-out mill—both advantages, the practical value of which cannot be over-estimated.

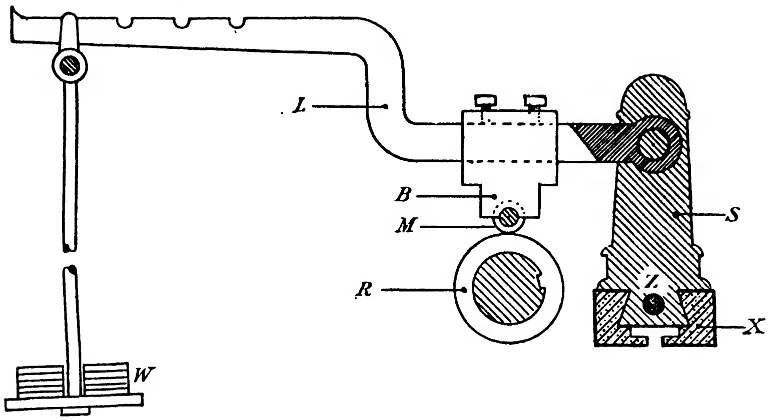


FIG. 34.—Diagrammatic sketch of engraving machine.

When a multicolour pattern is to be engraved by machine, it is of course necessary to engrave a separate die for every distinct colour. The dies must be of exactly the same dimensions; but the corresponding mills made from them may vary, so long as their circumferences are a multiple of those of the dies and a divisor of those of the rollers. The rollers, of course, are all of the same diameter and length. Formerly each succeeding roller of a multicolour pattern was made slightly larger than the one preceding it in the machine, so as to allow for the stretching of the cloth as it passed through the machine; but this arrangement had the drawback of requiring the rollers to be always worked in the same order, and was consequently abandoned, as more bother than otherwise; for it is often necessary, when many combinations of colour are printed to one design, to reverse the order in which some of the rollers are worked, for the purpose of preserving, as much as possible, the purity of the paler and more easily soiled tints, it being a principle in printing that the more delicate colours must be applied to the cloth before the darker (or " dirty ") colours. The cause of the soiling of delicate colours in machine printing was touched upon in the opening discussion on the relative merits of block printing and roller or machine printing, and nothing more need be said about it here, except to mention that it is a well-ascertained fact, known to all practical men, that a film or scum of dark colour on the *surface* of a light colour is much more easily removed in washing than if it occurred under the light colour—that is to say, if the light colour were printed on cloth already stained by passing under a dark roller. In the latter event the pale shade is irretrievably spoilt, it being practically impossible to remove the underlying dark tint without removing the light one along with it. For this reason rollers are nowadays usually made of the same size for a given pattern, so as to allow of their being changed about as required.

The only exception to this rule is the " blotch " or background roller, which

is still frequently made a little larger than the others, in order to fill up any vacant spaces due to stretching, and which cannot well be worked anywhere but last, on account of the mass of colour it puts on the cloth. If it is worked in a pale tint it is often preceded by a plain roller, interposed between it and the others. This plain roller works in a colour box containing starch paste, or gum, and serves to remove most of the superfluous or "top" colour from the cloth before it reaches the blotch. It is commonly known as the "starch" or "gum" roller; and its use is not confined to any one place in the machine, it being interposed wherever its action will be beneficial.

Pantograph Engraving.—Pantograph engraving is based upon a principle entirely different from that of either hand engraving or of machine engraving: the pattern is neither cut out with a graver nor indented by a mill, but is *etched* upon the roller by means of nitric acid or ferric chloride. For this purpose the roller is evenly coated with a thin film of a hard-drying bituminous varnish, and then the pattern is transferred to it with a diamond point which cuts through the varnish, at the same time laying bare the copper wherever it touches. On placing the roller in the etching bath, the nitric acid only dissolves out or etches the exposed parts, the film of varnish protecting all those portions that are intended to remain white in the subsequent printing. But the distinguishing feature of pantograph engraving is not in the application of the well-known process of etching to the engraving of printing rollers, but in the method of transferring to the *rounded* surface of the roller at one operation any required number of the repeats of a design, one *single* repeat of which is engraved, on an enlarged scale, upon a *flat* zinc plate. Two types of machine are used for this purpose—the curved-table and flat-table machines—but both are so intricate in construction that it would be hopeless to attempt to describe their mode of action in detail without an elaborate set of working drawings or an actual machine to refer to. It is therefore impossible to do more than to touch briefly upon the process of pantograph engraving, and to refer those who may desire fuller information to the special literature of the subject.

The first pantograph machine employed consisted of a simple modification of the rhomboidal arrangement of levers well known to draughtsmen as the pantograph. It never gained any measure of commercial success, however, and was soon discarded, not that it was altogether too limited in scope, but because the style of design then in vogue was better engraved by other means. In 1854 Rigby made the first curved-table pantograph used in Europe. It was constructed on the lines of the American invention of Whipple, who had replaced the system of levers by an ingenious contrivance based on the fact that if a large wheel and a small wheel are fixed to the same shaft and revolve together, a point on the circumference of the large wheel will cover a greater distance than a corresponding point on the circumference of the small wheel. The distance travelled by a given point on each wheel is, of course, 3·1416 times the length of its diameter, and consequently a 5-inch wheel would cover 15 inches (in round numbers) while a 1-inch wheel would only cover 3 inches; that is, the ratio varies in direct proportion to the respective diameters of the two wheels. The rotary movement of the wheels transformed into linear movement and communicated by suitable means to diamond tracing-points at once afforded a means of reducing the width of the lateral repeats of a design as much as desired, and a modification of the same principle, in which the roller itself plays the part of the smaller wheel, provided for an equal reduction of the vertical repeats. This improved machine of Whipple and Rigby being easily applicable to a wide range of styles, was at once adopted by the leading engravers, and, with a few additions and refinements, is still extensively used.

The more convenient and less cumbrous *flat-table pantograph* was invented by Shields in 1857, and embodied an ingenious and entirely novel method of reducing or varying the dimensions of the pattern transferred to the varnished roller. Its principle is somewhat difficult to describe in words, but it may, perhaps, be best explained by saying that it is based upon the observation that a body starting out from and moving in a direction oblique to a given straight line, travels along the hypotenuse of a right-angled triangle, one side of which is formed by the given straight line, and the other by dropping a perpendicular, from the final point of rest of the body, on to the given straight line. The ratio between the lengths of these two sides of the triangle varies according to the inclination of the hypotenuse, and, consequently, by altering this latter it is possible (within limits) to make one side any desired fraction of the other. A glance at fig. 35 will make this point clear.

Let *a b* be the given straight line. Then a body X travelling obliquely from *b* to *c* will cover, laterally, a distance equal to *a b*, and at the same time will obviously rise a distance equal to *c a* (or *d b*); and if *c b* be inclined at an angle of about $13\frac{3}{4}°$, the line *c a* will be four times less than the line *a b*. In practice, this principle is worked the other way about; that is to say, the body X moves perfectly horizontally along a fixed cross-bar below, and in a groove cut in an inclined and movable lever above, the result being that the inclined lever travels backwards and forwards according as the body X is moved to the right or to the left; and the distance the lever travels always bears a definite relation to its angle of inclination and to the amplitude of the movement given to X.

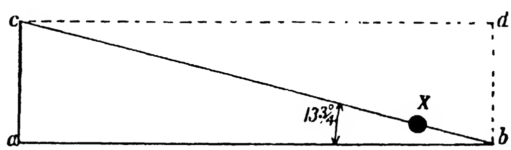


Fig. 35.—Principle of the flat-table pantograph.

In a flat-table pantograph machine two such sliding levers are employed—one to provide for the horizontal lines of the design, and the other for the vertical lines—and as their motion is compounded through the medium of a sliding arm which actuates them, either independently or both together, it is possible to reproduce on a smaller scale any kind of line whatsoever, be it vertical, horizontal, oblique, or curved. For this purpose the sliding arm is furnished with a tracing point for going over the design, and the inclined movable levers are connected with diamond points which bear on the varnished roller and cut a reduced replica of the design thereon through the film of varnish, thus laying bare the copper in readiness for the etching bath.

Figs. 36 and 37 represent a section and plan of a flat-table pantograph machine. They are stripped of detail, and must be taken as purposely exaggerated, to illustrate more clearly the working of the machine.

The parts are numbered and lettered as follows:—(1) is the framework of the machine, to which the various fixed rails and bars are attached; (2) the table upon which the design to be transferred to the roller R is laid; (3) the tracer-rod, carrying the tracer 4 at one end of it, and at the other attached to the bar 7 which runs on the flanged rollers *m* across the carriage 8, which in turn runs on similar rollers *a*, *a*, *a* on the fixed bars *b*, *b* at each side of the machine. The tracer-rod 3 passes freely through the bar 5 and between the guides 6, which always maintain it at right angles to the bar 5. From the carriage 8 an arm 9 extends upwards, carrying the stud 10 which works freely, but without side-play, in a groove cut from end to end in the lever 11. This lever is attached by an arm 12 to the cross-bars 13, 13, running on the rollers 15, 15, along the fixed rails 16, 16; and it may be adjusted at any desired angle, in reference to the tracer-rod, by means of the slotted boss and set screws 14, 14. When thus

inclined its groove forms an inclined plane, against which the stud 10 acts when the carriage 8 is pushed backwards and forwards by the tracer-rod 3, the result of this motion being that the lever 11, and with it the two cross-bars 13, 13, are moved transversely a fraction of the distance travelled by the carriage 8. The diamond points are supported on tool-carriers rigidly fixed to the bars 13, 13, and consequently move along with them, scratching a line through the varnish on the roller R at the same time. The bar 5, running on the rollers *f* on the fixed rail *e*, is provided with a stud 23, which works in a groove cut longitudinally in a second inclined lever 22, exactly like the lever 11, in that it can be fixed at any suitable angle by means of the boss and screws 21. This lever 22 is connected by the arm 20 to the cross-bar 19 of the carriage 18, which runs on the fixed rails *d*, being supported thereon by the rollers *c*. The varnished

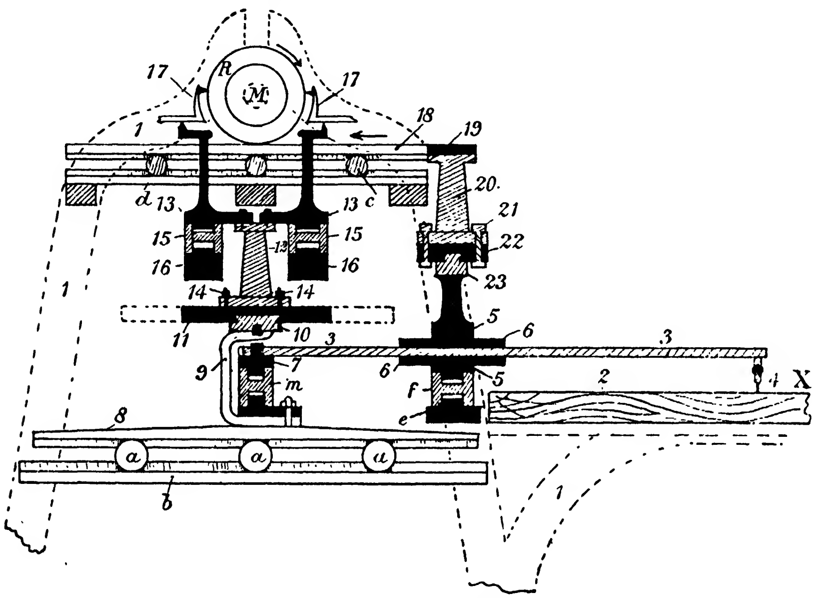


FIG. 36.—Section of the flat-table pantograph.

copper roller R is mounted on the mandrel M, which turns in sliding bearings fitted into the two slots at the top of each side of the framework ; and as the ends of the roller R rest in frictional contact with the side bars of the carriage 18, the roller revolves every time the carriage moves, and is scratched circumferentially by the diamond points which rest against it.

In using the pantograph machine, the design must first be enlarged and engraved upon a zinc plate. This may be done either by photographing it directly upon a prepared zinc plate, or by placing it in a camera-obscura which throws an enlarged image of it upon a piece of paper placed on a flat table in a dark room. The enlargement is traced, transferred to the zinc plate, and engraved thereon by hand, care being taken to cut the lines smoothly so that the tracing-point will meet with no obstruction to its passage along them. The plate is then placed in position on the table 2 (figs. 36 and 37), and after affixing on the bars 13, 13 a number of diamond cutting points corresponding to the number of side-repeats desired, the operator, seated at X, goes over every line of the pattern on the plate with the tracer 4, thus transferring to the roller R a series of reduced facsimiles of the same. The tracer is hinged on the rod 3 for

convenience and whenever it is lifted off the plate the diamond etching points are also moved out of contact with the roller by means of a foot-lever, not shown in the diagram. The position of the levers 11 and 22 being as in figs. 36 and 37, it is evident that every time the operator pushes the rod 3 away from him the lever 11 will be pushed to his right, and the diamond points will therefore cut a line through the varnish on the roller from left to right, in the direction of its length and parallel to its axis; if he pulls the rod 3 towards him, the reverse effect is, of course, produced. On the other hand, if he moves the rod 3 horizontally to the right, the lever 22 will be pushed away from him, and with it the carriage 18, thus causing the roller R to revolve, or rather partly revolve, in the direction of the arrow (fig. 36), and against the diamond tools 17; if the rod is moved to the left, a line is cut on the roller in the opposite direction.

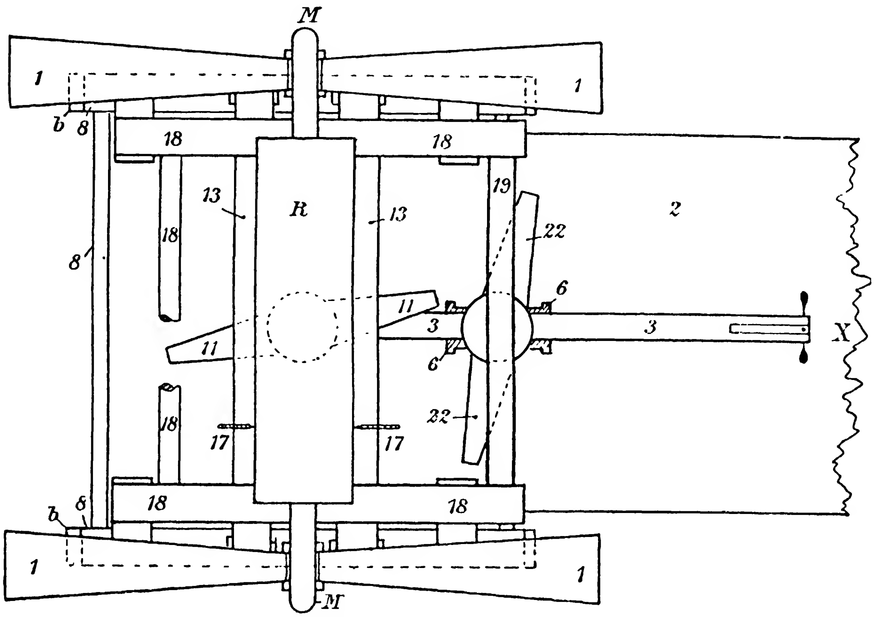


FIG. 37.—Plan of the flat-table pantograph.

When the pointer is moved obliquely or round a curve, the lateral movements of the diamond tools and the rotary movements of the copper roller are compounded, and the line cut on the roller is an exact reproduction in miniature of the line followed by the tracer on the zinc plate. In this way any kind of line or form whatsoever can be transferred from the flat surface of the table 2 to the rounded surface of the roller R, and that without any distortion. From the foregoing it will be seen that horizontal and vertical lines on the zinc plate change their positions on the roller, becoming respectively circumferential and lateral, thus reversing the "run" of the design by making the side repeats vertical, and the vertical repeats horizontal. Fortunately this is easily remedied by simply turning the engraved zinc plate half-way round on the table before commencing to transfer the pattern to the roller—the repeats then coming in their proper places. When a pattern is required to repeat more than once round a roller, it is usual to arrange the requisite number of diamond points around its circumference, but the same effect can also be obtained by using only one line of points (tools), the position of the roller being altered from time to time according to circumstances.

For multicolour patterns the whole design is engraved on a single zinc plate and is then coloured up like the original; this is for the guidance of the pantographer, and not only enables him to pick out and trace just those parts of the pattern that are required to be engraved on each separate roller, but also ensures that each roller will fit exactly to all the others over which the pattern is distributed, according to the number of colours it contains. Suppose, for example, a design was drawn up in red, pink, yellow, and dark and light greens. An enlarged copy of it would be engraved on a zinc plate and coloured in these colours; the pantographer would then place a varnished roller in the machine and transfer to it, say, all the red parts, by simply following with his tracer the outlines of the red objects on the plate; then, without altering the adjustment of the machine, he would replace the finished red roller by one intended for printing the pink portions of the pattern, and after transferring these latter would proceed to deal, in precisely the same way, with the three remaining rollers for the yellow and two greens. The five distinct colour elements of the complete design engraved on the zinc plate are thus abstracted and transferred to separate rollers, to be afterwards re-combined on the cloth during the subsequent printing process. All the five rollers being made from one single plate (Fr. *planche mère*) under exactly the same conditions, the certainty of their impressions fitting their allotted spaces in printing is much greater than if it were necessary to engrave a separate plate for each colour in the pattern; and it is this certainty, coupled with the speed of production, that renders the process of pantograph engraving so valuable an adjunct in textile printing.

After leaving the pantograph machine, the rollers are etched in a bath of nitric acid. The acid is contained in a shallow trough of stone, and the rollers are revolved therein until the pattern is etched out to the requisite depth. The strength of the acid and the length of immersion are largely questions of practical experience, but it may be noted that if the action of the acid is too energetic the etched lines, instead of being smooth and even throughout, will be pitted. To avoid the liability to pitting, many additions to the nitric acid bath have been suggested—amongst them 12 per cent. to 20 per cent. of acetic acid—but it is questionable whether or no they are of any real value. Rollers etched in a mixture of nitric and acetic acids, used by one of the largest firms in England, are certainly remarkable for their clean, even lines, but whether this result is due to the beneficial action of the acetic acid or to the dexterity of the etcher is still a moot point. When sufficiently etched, the rollers are well washed in water, the varnish is cleaned off with benzine or turpentine, and, after any defects have been retouched by hand, they are ready for printing. If a roller requires re-etching, it is varnished again and given a short treatment in the acid; in fact, if the engraving is very deep, it is essential to do the etching in stages, re-varnishing between each, as otherwise the effect of "under-etching" would be produced—that is, the acid would eat its way under the varnish and give a line widening out as it got deeper. Such a line would give an impression in printing with ragged edges, and would be quite useless for most purposes.

Ferric chloride is now largely used for the etching of rollers. It acts more slowly than nitric acid, is more easily controlled, and is practically free from the tendency to under-etch.

Varnishing.—The varnishing of rollers is performed as follows:—A plain brass roller and the copper roller to be engraved are placed in a machine and revolved rapidly side by side; the thickish varnish—a mixture of Burgundy pitch, tallow, and Venice turpentine—is then poured on the brass roller and spread evenly over it by means of an inking roller (of glue and treacle melted together and cast in a mould), mounted on a frame and held in the hands of

the operator. When the varnish has become tacky, the "treacle" roller is placed in contact with the copper roller and transfers a thin film of varnish to its entire surface, the operation being continued and repeated until the film is thick enough to protect the roller thoroughly from the action of the acid. By this means an already etched roller may be re-varnished without the slightest fear of the varnish filling up, or even getting into, the etched lines.

The process of etching is not confined to pantograph work ; it may also be employed in combination with machine engraving. For this purpose a mill is used to indent the outline of the object ; the whole roller is then varnished and ruled, with a diamond point, with a series of parallel lines, at the angle and the distance apart required by the "scale" of the engraving. The outline and those portions of the roller not to be etched are then painted or "stopped" out with varnish, and the roller is finally etched, cleaned, polished, and trimmed up as usual.

In many modern pantograph machines the diamond points may be made to work in opposite directions to each other—a feature which allows of "turn-over" patterns being pantographed from a single repeat of the subject, engraved in one position only on the zinc plate. Other refinements of motion are also possessed by modern machines which render them applicable to a variety of purposes which cannot be mentioned here.

Stipple Engraving by Machine.—Stipple engraving, which is distinguished from ordinary engraving by being executed in punched dots instead of in cut lines, was, by reason of mechanical difficulties, formerly confined to hand work.

It was a tedious, expensive, and delicate process, and as first-rate stipple engravers were not common, the desirability of producing it by mechanical means had long been recognised.

So far as the authors know, the only successful solution of the problem is that embodied in the four principal patents of J. T. Rawsthorne for "Improvements in the methods and apparatus employed in engraving rollers for calico printing and similar purposes."[1] The process is carried out on an ordinary pantograph machine adapted to take the special apparatus devised for punching and drilling the stipple dots. This apparatus replaces the diamond points used in ordinary pantograph engraving, and, as the punches and drills act directly on the rollers or dies, neither varnishing nor etching is necessary. The fundamental basis of the process consists in the preparation of an improved zinc plate (termed the pattern plate) upon which an enlargement of the pattern is engraved in the customary manner. The plate is embossed, or rather indented, over its whole surface with a ground-work of dots spaced at a distance of 2 millimetres apart, the indentations being obtained by simply passing the plain zinc plate between the bowl of a printing machine and a steel roller with the dots raised in relief upon its surface. Each dot on the plate that falls within the limits of the parts of the pattern to be shaded represents a corresponding dot on the finished die. It will be observed that the dots, in this process, are equidistant, whereas in ordinary stipple engraving the gradation is obtained by varying not only their size and depth, but also their distance apart. In practice this difference of method has no noticeable effect, as, with a diminution of five times, the dots come so close together that the necessary gradation can be got easily by merely varying their depths and diameters.

The mechanism of the punching and drilling attachments used for these

[1] English patent No. 6149 (1907) for embossed plate.
" " " 6150 " " punch apparatus.
" " " 12679 " " drill apparatus.
" " " 4189 (1908) " flat die.

purposes is too complex to deal with here, but a full description of it will be found in the several patent specifications already cited. In principle, however, the attachments are comparatively simple, and the following résumé will perhaps convey some idea of their construction and operation :—

1. The punching apparatus may be regarded as a pivoted hammer, into the head of which a steel punch is inserted. It takes the place of the diamond points used in ordinary pantographing, and is actuated in exactly the same way, viz. being alternately raised out of contact with, and allowed to drop upon, the steel die by means of a foot-lever. The pivoted handle or lever of the punch is provided with an adjustable weight-carrier consisting essentially of an upright rod fixed in a steel block, which slides in a groove machined from end to end of the lever. Any required number of annular lead weights may be placed on this rod, and by varying its position along the lever any desired force may be imparted to the blow of the punch—the nearer the weight to the pivot, the lighter the blow and the smaller the dot, and *vice versa*.

2. The drilling apparatus is intended to supplement the work of the punch. It is preferable in most cases to enlarge and deepen the punched dots or pins, by drilling, because heavy punching raises more burr than is desirable. The apparatus is a delicate piece of mechanism and requires to be most accurately machined in all its parts. The slightest wobbling of the point of the drill causes distortion of the " pins," and renders the work defective. The drill itself is made of the finest steel, and upon its grinding to a three-sided pyramid, with the point in the dead centre, depends the perfection of the engraving. It is mounted in a drill-stock, and is caused to revolve, through the medium of bevel gearing, by means of a rack-and-pinion motion actuated by a lever working in connection with the ordinary raising bar and foot-lever of the pantograph machine. The number of revolutions performed by the drill may be controlled by an ingenious device which varies the travel of the rack ; the latitude is usually between five turns and half a turn, and this is found to be ample for all classes of work. The punching and drilling appliances are interchangeable, and so accurately built is the whole machine, that any series of punched dots can be drilled, subsequently, from the same pattern plate without the slightest fear of mistake.

In general the procedure of engraving stipple patterns by machine follows closely on the lines of the older methods of pantograph engraving. An instance will suffice to indicate the differences. Thus, if the dark and medium shades of pink and olive in a rose pattern were required in stipple, the following sequence of operations would be carried out :—

1. The whole pattern in full colour would be drawn and engraved on the special pattern plate--five times its proper size.

2. The plate would then be fixed on the table of the pantograph machine and suitable dies would be placed in position under the punching apparatus.

3. The engraver would select one colour—say the dark pink—and proceed to divide it into zones by drawing pencil marks over it according to the shape assumed by the gradations.

4. He would then adjust the weight of the punch and commence to engrave (say the darkest shade) by placing the pointer in each dot in turn, pressing down the foot-lever and allowing the punch to fall on the die for every fresh application of the pointer.

5. When every dot in the darkest zone had been dealt with in this way, a simple turn of the adjusting wheel would alter the position of the weights on the punch, and, by bringing them closer to the pivot, would reduce the force of its impact on the die, thus giving smaller and shallower dots. The second zone of shade would be engraved with this lighter weight. A third, fourth,

and up to a seventh or more alterations of weight might follow, the number depending on the zones into which the design had been divided and also upon the class of gradation required.

6. After the punched die had been polished, the punch would be replaced by the drilling apparatus, and such of the dots as required it would be drilled to size and depth. The number of turns given to the drill would be determined by the zones on the pattern plate in precisely the same manner as was the weight of the punch— in fact the whole operation is identical except that drilling supersedes punching. As a rule it is unnecessary to drill the outer zones of stipple; punching alone is sufficient for the more delicate. The medium pink and the two olive dies in the pattern would be treated similarly.

After drilling the dies are hardened and used for the preparation of mills in the manner already described elsewhere.

By a simple modification of the pantograph machine it is possible to engrave flat steel dies in an equally perfect way. With a single flat die any number of mills may be prepared with the object in different positions, by the simple expedient of varying its position in the clamming machines.

The above-described methods of stipple engraving are successfully operated in the works of Messrs E. Potter & Co. Ltd., of Dinting (a branch of the Calico Printers' Association), and their value has been fully demonstrated by the experience of many years. Dies produced by their means are turned out in less than half the time formerly occupied by the method of hand engraving, and their adoption has further rendered it possible to dispense with the costly hand labour hitherto necessary for this class of work. Moreover, in addition to effecting these two notable economies, the quality of engraving they yield is superior in point of precision, accuracy, and ease of repetition to anything that can be produced by the average hand engraver.

MODIFICATIONS OF THE CYLINDER PRINTING MACHINE.

Any description, however slight, of the various methods of printing textiles would be incomplete without some mention of the modifications and improvements that have been effected in the cylinder machine with a view to adapting it to styles of work that formerly were either impossible to execute, or that required to be filled in afterwards by hand block printing. Of these modified machines the two most important are the "Duplex" machine and the "Sarrie" "intermittent" or "jumper" printing machine. The duplex machine prints *both sides* of the cloth in the same pattern at one operation, the printed parts on one side coinciding exactly with those on the other side. The sarrie or jumper machine allows a certain number of rollers to print a certain predetermined length of cloth, and then to recede out of contact with, or jump away from, the pressure cylinder; simultaneously with this latter motion a second set of rollers moves up against the cylinder and prints that portion of the cloth that has escaped the first set. The second set then jumps away in turn, and the first set returns to its original position and prints a further length of cloth, and so on without intermission, the two sets of rollers printing their portions of the design alternately until the whole cloth is finished.

The Duplex Machine.—The duplex or reversible printing machine is really a combination of two ordinary cylinder printing machines, arranged one behind the other, and each provided with its own blanket and back greys.

The only real connections between them are the motive power which drives them both, and the cloth, which, when printed on one side on the hinder machine, passes directly round the cylinder of the front machine and is printed on the other side. In all other respects the two machines may be considered

as distinct, and they are worked as such, except in so far as the pattern on one side of the cloth must hit off exactly that on the other side—that is to say, that a pin pushed through the point of a leaf on one side must come out at the corresponding point of the same leaf on the other side. In order to facilitate this correspondence of the two patterns the crown wheel of the back machine is frequently made in the form of a huge box-wheel, so that if all the rollers of the back pattern are in perfect fit with each other, but *not* with the front pattern, they can all be moved an equal distance up or down by simply turning the adjusting screw of the crown box-wheel, and that, too, without upsetting their

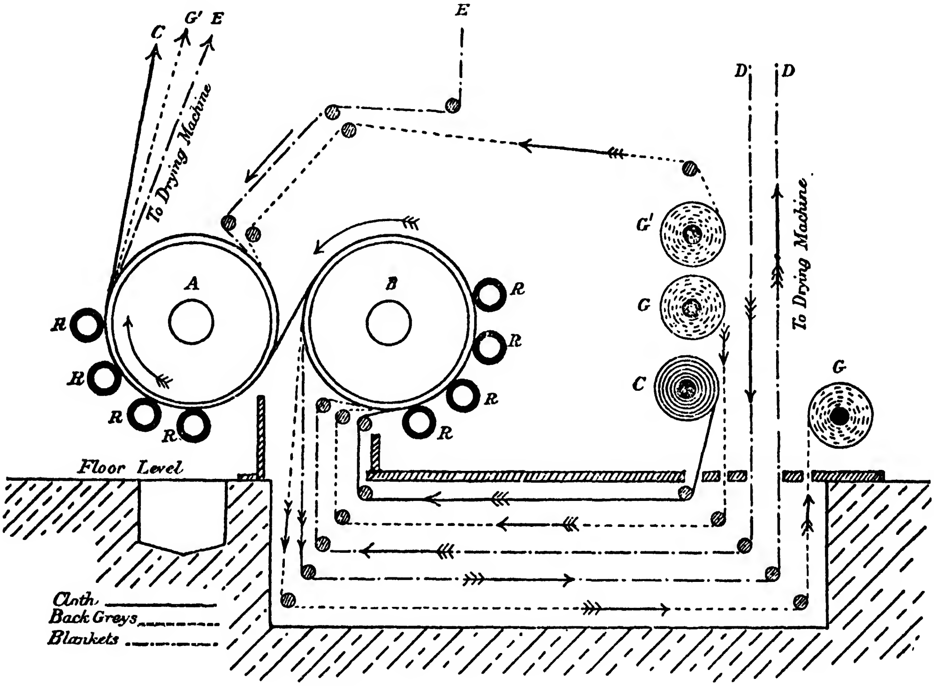
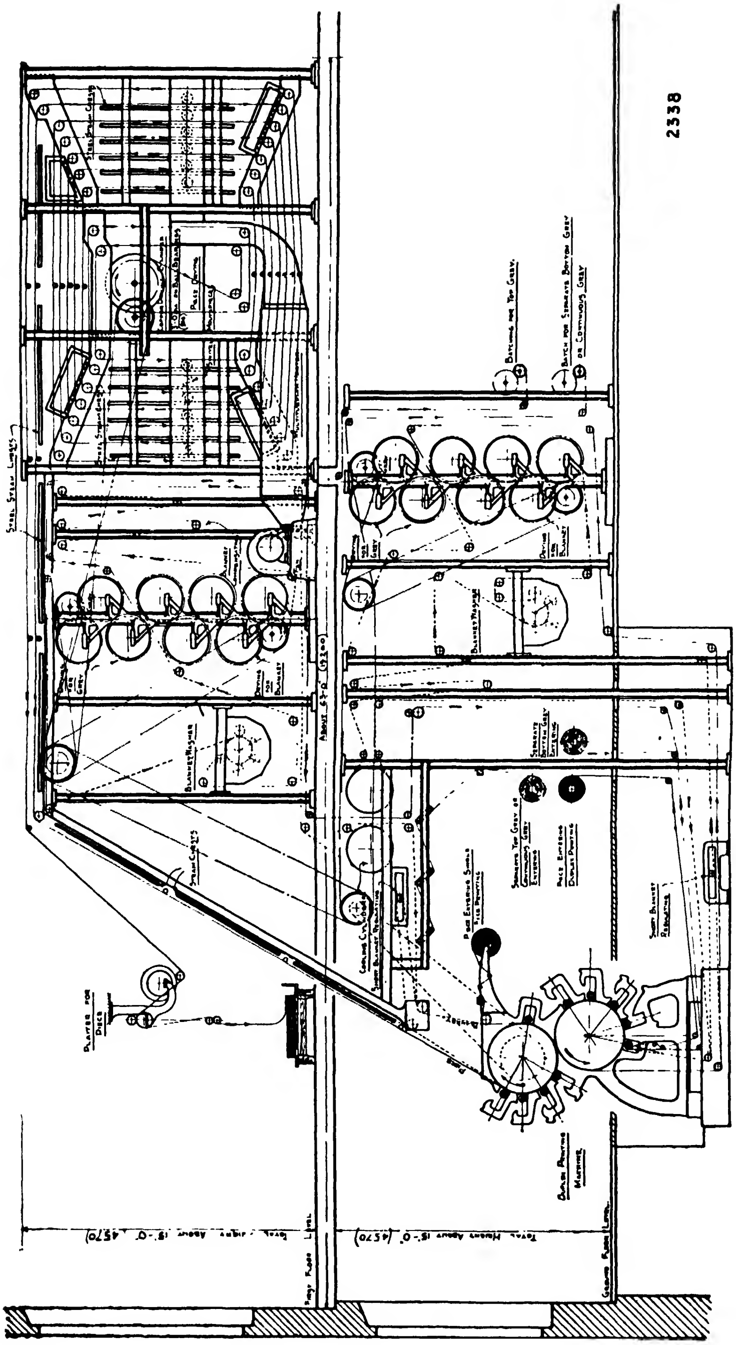


FIG. 38.—Duplex machine (section).

fit. Fig. 38 illustrates the disposition of the parts of a four-colour duplex machine.

A is the front cylinder ; B, the back cylinder ; C, the roll or " set " of cloth to be printed ; D, D, the blanket of the back cylinder ; E, E, the blanket of the front cylinder ; G, the back grey for back cylinder ; G′, the back grey for front cylinder ; and R, R, R, R, the engraved printing rollers. The boxes and doctors for each of these printing rollers are not shown, but they are arranged in precisely the same manner as in ordinary single-side printing machines. The cloth enters the machine from below, passing, along with the blanket D and the back grey G, under the feet of the printer ; in circulating round the cylinder B it becomes printed by the first four rollers R, R, R, R, and then passes on to the cylinder A, as shown in fig. 38, the printed side being next to the back grey G′ ; the second set of four rollers R, R, R, R then prints the other side thus exposed, and the cloth passes forward in the usual way to the drying apparatus, to be afterwards treated as an ordinary print in the subsequent processes. The direction taken by the cloth, the blankets, and the back greys is clearly indicated by the arrows in the diagram. The blankets are of the usual endless



Duplex Printing Machine with Steam Chest and Hot-air Drying Apparatus.

[*To face p.* 87.

type, and circulate continuously through the drying machine and round their respective cylinders. The two cylinders A and B are geared together and driven by an engine common to both. The gearing is arranged so that one of them can be used as an ordinary machine when not required for duplex work. Goods printed on both sides are generally known as "reversibles."

A slightly different form of duplex printing machine, manufactured by Messrs. Mather & Platt Ltd., is illustrated, together with its drying arrangements, in Plate IV. The pressure cylinders, in this case, are mounted one above the other instead of one behind the other—a disposition which is more convenient for the printer and also occupies less floor-space. It will be noticed that the two wash-blankets and the two back greys are all dried by passing over or round steam-heated cylinders, whereas the printed piece itself is dried by passing between a series of steam-heated chests situated in an enclosed drying chamber heated by hot air blown in by a fan through a multitubular heater. In this way the various defects that are liable to arise when wet colours are hard-dried in actual contact with hot metallic surfaces are avoided. The printed piece emerges from the machine dry, but not baked, and with its colours in a condition well adapted to react properly in the various after-treatments that may be necessary to bring about their full development.

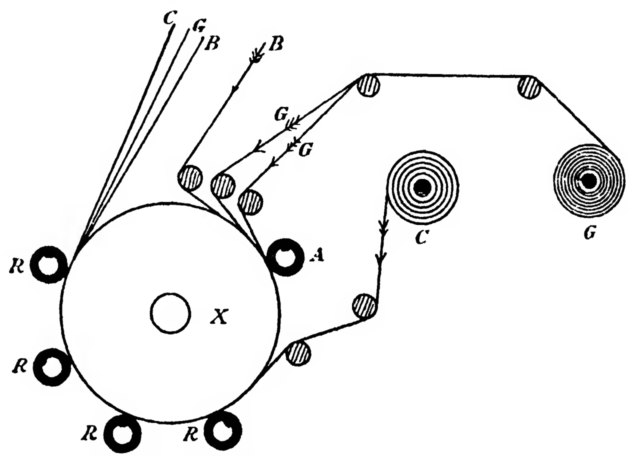


FIG. 39.—M'Nab's method of duplex printing.

Another and older method of printing both sides of the cloth was invented by M'Nab, and is carried out on an ordinary printing machine. In this process the back grey is printed before it meets with the cloth, and consequently, when the two pass together under the rollers that print the cloth, the pressure they are subjected to causes the cloth to take up a goodly portion of the colour printed on the grey, and thus to receive an impression on the back. Fig. 39 will sufficiently illustrate M'Nab's process without further description.

X is the cylinder; A, the printing roller for the grey; R, R, R, R, the rollers for printing the face of the cloth; G, G, a double grey; C, the cloth to be printed; B, the blanket. It will be seen from the above diagram that the grey is printed first; that the back of the cloth then comes in contact with the printed side of the grey, and that it must of necessity receive an impression therefrom. The front of the cloth is printed in the usual way. The double grey is employed solely for the purpose of keeping the blanket clean, and can be dispensed with in the case of wash-blankets. Practical difficulties render M'Nab's process unsuitable for printing reversible effects in more than one colour on the back; but for this purpose it is well adapted, and is still largely used in some works, especially for thick materials like flannelettes, on the back of which it is frequently required to print a fine all-over stripe pattern in some colour that will harmonise with the design on the face of the cloth.

In all duplex work, provided the cloth be sufficiently thick and the colours

properly prepared, it is possible to print the two sides of the cloth either in two different patterns or in two different colour combinations of the same design. This style, however, requires to be carefully executed if success is to be attained. The colour must be thick, and the pressure of the rollers against the cylinder as slight as is consistent with a good impression; otherwise, when two different designs are printed, either one or both is almost certain to show through the cloth, or if two different colourings of the same pattern are printed, their colours will penetrate through the cloth, and by intermingling will produce, in most instances, a most unpleasant, uneven, and muddy effect.

The Intermittent or Jumper Printing Machine.—Intermittent machines are used for the printing of sarrees or scarves, which may vary in length from 2 yards to 12 yards or more. The characteristic feature of the sarree is that it must terminate, at each end, in a wide cross-border of different design to that of the intervening portion, which is known as the "filling"; hence the necessity for printing intermittently and not continuously as in ordinary printing. In order to do this, two sets of rollers are employed, each set being brought, in turn, into contact with the cloth on the pressure bowl of the printing machine and held there by strong steel springs. As soon as the printing of one set, say that of the cross-border, is completed, its rollers are withdrawn or "jump away" from contact with the bowl, the other set ("filling" rollers) simultaneously coming into action and, after printing its predetermined length of cloth, being similarly withdrawn. Thus cross-border and "filling" are printed alternately, the rollers of the one being out of contact with the cloth for the length printed by the rollers of the other.

The means employed for throwing the printing rollers in and out of action in "jumpers" are both numerous and varied in principle. Some makers make use of lugs or cams fixed on an endless chain, which revolves with the machine, and in contact with rods which act directly on the bearings of the rollers, forcing them back every time a lug passes under them; others, again, employ revolving cams which act, through a system of levers, in just the same way; and yet others force the rollers into contact with the cylinder by means of steam or compressed air acting on a piston the rod of which communicates with the roller bearings, and moves them backwards and forwards at regular intervals.

In practically every type of intermittent machine the length of cloth printed and the length allowed to pass unprinted by certain rollers is determined by cams, which act either directly, or through levers, or by opening steam or compressed-air valves, upon the rollers. Machines of the older type, with heavy endless-chains carrying large direct-acting lugs or cams, are no longer made, though a few are still in existence. They have been superseded by other cam systems in which the control and timing of the to-and-fro movements of the printing rollers, relative to the cylinder or bowl, are effected either by adjustable or interchangeable revolving cams working on a counter-shaft and acting through levers on the sliding bearings of the rollers, or by light measuring chains running on sprocket wheels and fitted with slides and fingers which operate and control the working of the cams. In this latter system, the length of the *filling* of the sarree may readily be altered by lengthening or shortening the measuring chains, and so perfect is the timing that the pattern of the cross-border registers exactly with that of the filling. Steam and compressed-air machines are later developments of the same idea of intermittent printing, but, so far, they are no more than competitors of the purely cam machines, though it is quite possible that, in course of time, they may replace the latter, since the wear and tear on their valve-opening cams is much less than that on those cams which have to act more or less directly against the thrust of powerful steel springs in the roller bearings or "nips." That cams should be of the right size

is one of the most important factors in good sarree printing and it is, therefore, a great recommendation to any system if it can be shown to prolong the life of the controlling cams. It is also claimed for the use of steam or compressed air as a means of moving the rollers that it reduces considerably the force of the shocks occasioned by the rollers as they jump into and out of printing contact with the cylinder, an advantage which, by lessening the vibration of the machine, adds, in no small measure, to the facilities for keeping the various rollers in register.

Rubber Bowl or Squeegee Machine.—Another modification of the cylinder machine used for printing on one side of the cloth only is the SQUEEGEE MACHINE of Messrs. Sackville & Swallow. The great advantage claimed for this machine is that it dispenses with the necessity for lapping, blankets, and back greys, their place being taken by a cylinder covered with a thick layer of india-rubber, which does duty for all, and which is kept constantly clean by being washed at every revolution of the machine. In other respects the squeegee machine is worked in the usual way. Fig. 40 is a section of it, showing all its essential features—the washing arrangement and india-rubber pressure bowl, etc.

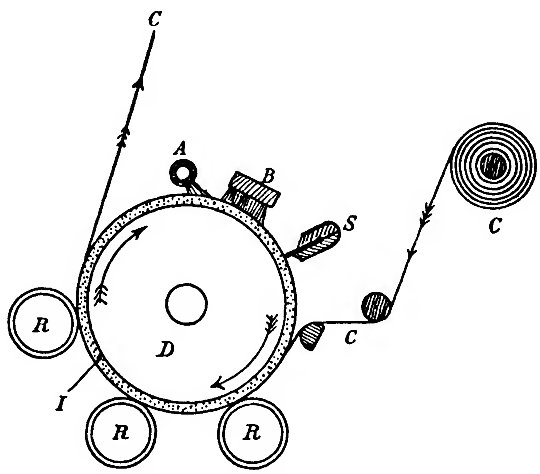


FIG. 40.—Squeegee printing machine.

The cloth to be printed, C, enters the machine at the point shown and passes round the cylinder D covered with the layer of india-rubber I, and between it and the engraved printing rollers, R, R, R, in the ordinary manner. Any colour that may have penetrated through the cloth on to the surface of the cylinder, D, is removed by means of the washing tackle A, B, S, which consists of a spirt pipe, A, delivering a constant stream of warm water; a reciprocating brush, B, which scrubs the adhering colour off the face of the cylinder; and the india-rubber squeegee, S, which effectually removes the excess of water, leaving the surface of the cylinder perfectly clean, and sufficiently dry to allow the printing to be proceeded with without fear of the colours running into each other. The squeegee machine is said to yield excellent results in the hands of its inventors, in whose works it is installed, but so far it has failed to recommend itself to the majority of calico printers, who find the older machine better adapted to the various styles of work with which they have to deal. So long as the india-rubber covering of its cylinder is in good condition, it is possible that the squeegee machine may be worked much more economically for three- and four-colour patterns than the ordinary machine, the working expenses of which are augmented by the necessity for increased drying accommodation, by the cost of blankets, lapping, and greys, and by the extra time and labour required in their manipulation. On the other hand, india-rubber-covered bowls of all descriptions are liable to rapid deterioration under pressure, and, from what has already been said respecting the conditions of calico printing, it is easy to see that once the bowl of the squeegee machine is damaged or becomes uneven from constant use, it

immediately becomes quite useless for its purpose, and must be either repaired or replaced. It is well known that repairs are rarely satisfactory, and that in the long run it is always best to re-cover entirely a rubber bowl; so that possibly the cost of maintaining the efficiency of a squeegee machine may more than counterbalance the gain derived from its doing away with blankets,

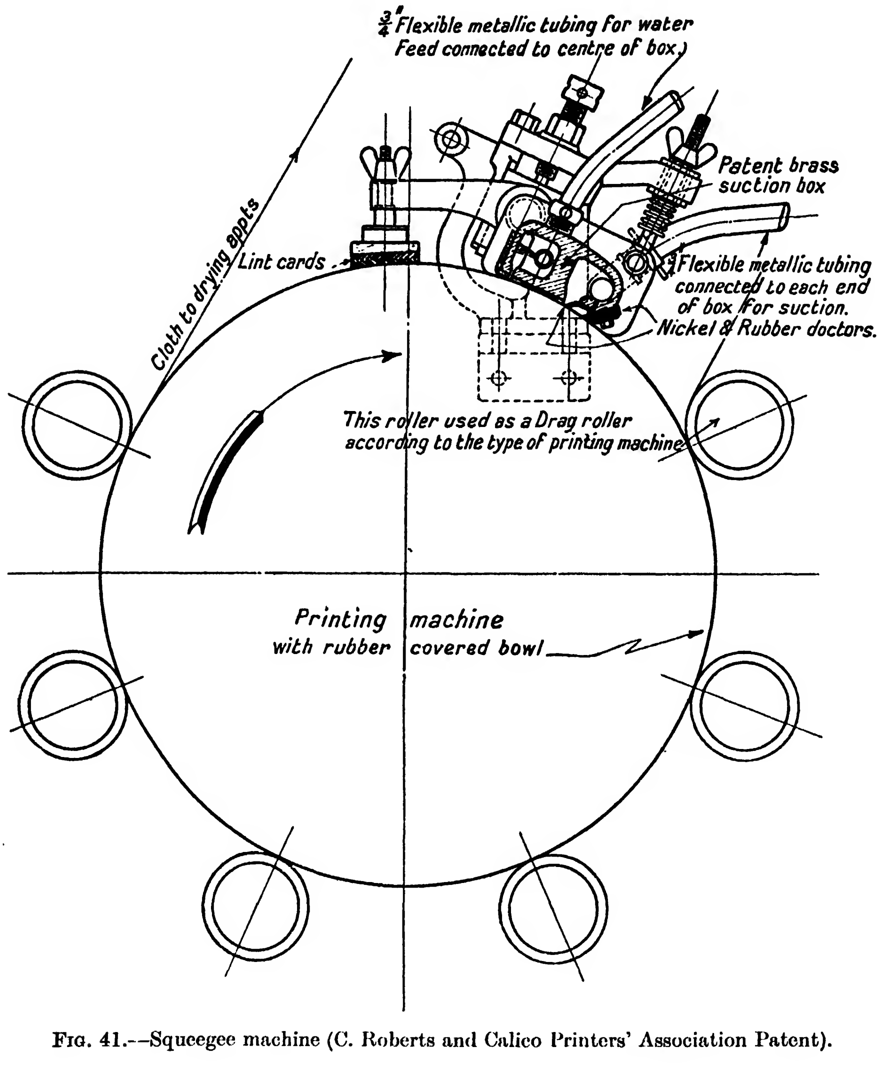


FIG. 41.—Squeegee machine (C. Roberts and Calico Printers' Association Patent).

back greys, and lapping, for rubber-covered bowls of large size are expensive items in any machine. At any rate, the principle of the squeegee machine is scarcely applicable to machines printing from six to twelve colours at a time. In the first place, the large amount of space taken up by the washing apparatus would make it necessary to employ cylinders of abnormal size, and these, covered in rubber, would be very costly; secondly, the enormous sum-total of the pressures of the various rollers would, judging by the analogy of

ordinary rubber squeezer bowls, very soon cause the rubber to detach itself from its iron bed, and thus render the cylinder utterly useless ; and thirdly, the rollers would always have to be wider (or longer) than the cylinder, to prevent the rubber covering from being crushed or squeezed outwards towards the edges, and gradually accumulating there, until it finally interfered with the regularity of the printing. As in many (probably most) cases the printing rollers are shorter than the width of the cylinder, the employment of squeegee machines would add considerably to the cost of production in all works where thousands of patterns are in constant use, and thus the extra capital sunk in copper alone would probably absorb the gain in other directions. Add to all this the fact that every additional roller increases the risk of damage to the bowl, and it is easy to understand why the squeegee machine has not been more generally adopted.

An improved form of the squeegee machine, patented by C. Roberts and the Calico Printers' Association, Ltd., differs from the preceding type in the means adopted for cleansing and drying the rubber-covered bowl.

From fig. 41 it will be seen that the three separate elements of the older washing arrangement—spirt pipe, reciprocating brush and rubber doctor, all working in the open—are replaced by a single piece of apparatus in which their several functions are combined.

This apparatus, known as the suction box, consists of a long, narrow, and hollow brass casting, divided longitudinally into two chambers, one of which is connected with the water supply and the other with a suction pump. It extends across the full width of the rubber bowl, and its ends, or shorter sides, being machined to an arc of the same radius as the bowl, it fits the latter sufficiently closely to prevent the escape of water, and yet not so tightly as to interfere with its rotation. The two chambers are separated from each other, at the bottom, by a wide strip of corrugated metal (which takes the place of the brush); and the corrugations form the only means of communication between them when the suction box is adjusted and bolted into position on the sides of the printing machine. At the entrance to the second chamber —the suction chamber—a nickel doctor is fixed for the purpose of intercepting the bulk of the dirty wash-water drawn, through the furrows of the corrugations, from the first chamber along the surface of the bowl. In this way the work of the squeegee proper is reduced considerably, with a corresponding gain in efficiency. The front of the suction box is arranged to allow of a little clearance between it and the bowl so that the colour on the latter may not be scraped off by, and pile up in front of, the suction box, but pass into it and be washed off by the water and exhausted by the pump. The back of the suction box is formed by the rubber doctor, the action of which is the same as in the machine already described. Fig. 42 shows the section of the latest pattern of Roberts's suction box.

A, water feed-pipe attached to centre of the box ; B, water-supply chamber from which, through the passage C, the water is sprayed on the rubber bowl ; D, the exhaust chamber, into which the wash-water is drawn by the joint action of the rotation of the bowl, the nickel doctor E, and the suction pump connected to the pipe F. H is the adjustable rubber doctor, or squeegee. Any water that escapes past the doctor E is stopped by the squeegee H, and is drawn off into the suction chamber through the supplementary passage G. The portion of the suction box immediately under C is slightly out of contact with the bowl, as mentioned above, but any escape of water at this point is prevented by the travel of the bowl and the suction pump.

The corrugations on the flat underside of the chamber B (between C and E) are cut at an angle and their ridges lie on the bowl. In this way the use of a

brush is dispensed with and the water is evenly distributed over every part of the surface of the bowl.

At first the presence of lint interfered with the working of the suction box, but this drawback was soon obviated by fixing a strip of brass-wire card immediately in front of it, as shown in fig. 41.

All connections with the water feed and suction pump are made with flexible metallic tubing, so that these parts of the machine can be placed in any convenient position.

Many other forms and modifications of the printing processes have been suggested, and even introduced into practice, for special styles; but as they are not of general interest, an account of them must be looked for in the files of the various periodicals that are devoted to the review of current events and improvements in the dyeing and printing industries.

Before leaving the subject of methods of printing textile fabrics, it may be

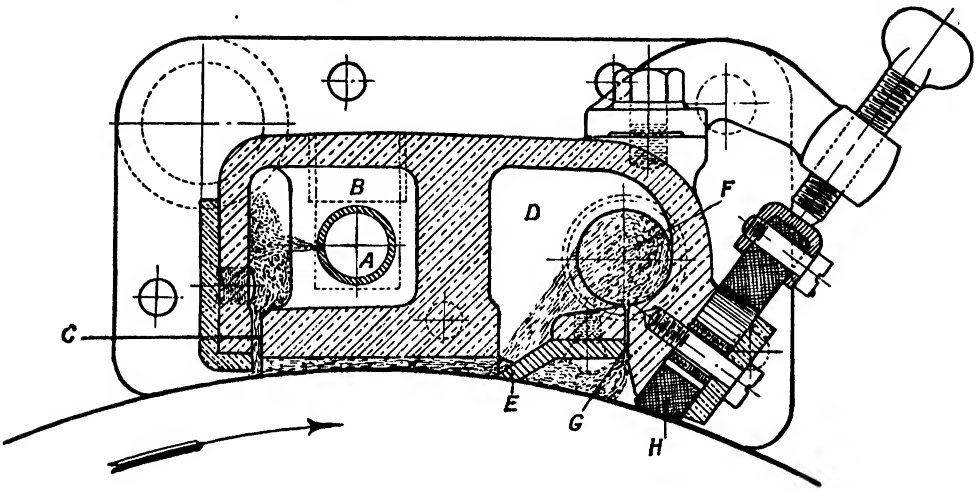


FIG. 42.—Roberts's suction box (section).

well to mention that all cloth for printing is wound on hollow wooden or iron shells, through which a loose iron centre or axle is passed when the roll is required for placing in the machine. The ends of this axle rest in slots prepared to receive them, and the cloth is simply unwound by being drawn through the machine between the printing rollers and the pressure bowl. On its way it passes under and over a series of tension rails, and over one or more scrimp rails, which free it from pleats and creases, so that it enters the machine stretched to its full width, and presents a perfectly even surface to the action of the rollers.

Defects Incidental to Roller Printing.—Apart from the actual misfitting of a pattern, which is not an accident, but due to carelessness, the principal defects to which patterns printed by machine are liable are the following:—

1ST, SCRATCHES.—These may be caused in many ways, but they are usually due to gritty particles (sand or metal) in the colour, which cut into the surface of the roller deeply enough to show themselves when the goods are fully developed. Scratches are remedied by burnishing.

2ND, SNAPPERS.—Large, ugly-looking double stripes of colour running up the piece are caused by some foreign substance getting under the doctor-edge and lifting it off the roller, thus permitting a large amount of colour to pass and

be transferred to the cloth in the form of a smudgy stripe. Snappers may be either long or short, according as the obstruction gets jammed between the roller and doctor, or works itself loose almost immediately; in either case it is advisable to stop the machine, to wash both doctor and roller, and to send the colour to be strained afresh. One of the commonest causes of snappers is due to loose threads from the cloth escaping under the lint doctor, and afterwards being carried up with the colour under the cleaning doctor, which they lift, with the result already described. Bits of dried colour, pieces of starch that have not been mixed in properly, and other hard bodies are all likely to give rise to snappers if they are allowed to remain in the printing colour.

3RD, LIFTS.—These are very like minute snappers, but they usually occur at regular intervals on the cloth, although they are sometimes veritable snappers, caused by the passage under the doctor of a minute particle of grit. When they recur at regular distances, corresponding to the circumference of the roller, they will invariably be found to be caused by a particle of steel that has become embedded in the roller, and which, by projecting a little, lifts the doctor every time it passes under it, and so allows a small quantity of colour to remain upon the smooth, unengraved surface of the roller--colour which, of course, is transferred to the cloth.

4TH, STREAKS.—Streaks consist of fine lines or series of fine lines running along the piece in a direction more or less parallel to its selvedges, and they may result either from a scratch on the roller or from a snip in the doctor-edge. Both scratches and snips are mainly caused by grit in the colour, and not infrequently by the steel filings that have escaped removal when the doctor-edge was sharpened. A doctor-streak is easily distinguished from a scratch in the roller by its wavy appearance, which is due to the traverse motion of the doctor; streaks arising from scratches in the roller are always straight, unless it happens that the offending particle of grit sticks on the doctor, and is carried to and fro with it, thus cutting an undulating line on the roller. As a rule, a scratch of this latter description forms a broken line or streak, whereas a snip in the doctor gives a continuous line throughout. Streaks can only be remedied by either polishing the roller or re-sharpening the cleaning doctor.

5TH, SCUMMING.—Scumming is a term applied to the effect produced by the insufficient cleaning of the unengraved smooth surface of the printing roller —an effect which consists in the whole surface of the cloth being soiled by a film of one or more colours. Scumming may arise from any one of the following causes:—(*a*) a rough doctor-edge; (*b*) a badly adjusted doctor, the edge of which does not rest upon the roller sufficiently sharply to scrape off the superfluous colour; (*c*) a badly faced roller—that is, one with a rough surface which retains enough colour, after passing under the doctor, to soil the cloth in those parts which ought to remain unprinted by it; and (*d*) defective colour, which either obstinately resists the cleaning action of the doctor, or abrades the polished surface of the roller, or destroys the smoothness of the doctor-edge by acting upon it chemically or physically. Strong basic colours, colours containing much acid, badly ground pigment colours, and those, too, containing a large amount of solid matter or strong alkali, are all liable to act detrimentally in one or other of the above ways, and their preparation therefore demands the utmost care. In the case of printing pastes made up with energetic oxidising or reducing agents, and with strong alkaline lyes, it is frequently necessary to prepare the cloth with some substance capable of neutralising the action of the thin film of colour which always remains on the roller, even when the machine and colour are in the best condition it is possible to attain to in practice. Re-polishing the roller, re-sharpening of the doctor, or modifying the composition of the colour and re-straining it are all remedies

for scumming that are applied, according to the circumstances in which it occurs.

6TH, SCRIMPS.—These and doubled edges are simply creases in the cloth which pass through the machine, and, in preventing the colour from reaching the underlying parts of the cloth, show up as white places in the finished goods. As a rule, good scrimp rails of corrugated brass are all that is necessary to smooth out and stretch the cloth, but occasionally fine creases that have been dried in, on the drying-machines after bleaching, resist all attempts at removal in this way, and the only thing to be done in such cases is to wet out the cloth and re-dry it, either over the ordinary drying cans or on a stentering machine.

7TH, UNEVEN PRINTING.—Uneven distribution of colour takes place under many different conditions and manifests itself in various ways, all of which may be accounted for by some defect in either the cloth, the rollers, the colour, or the working of the machine. If light, granular looking, irregularly shaped patches are developed during the operations of steaming or dyeing, their occurrence may be put down in most cases to the presence of lime left in the cloth during the bleaching. Lime stains occur at irregular intervals, and are easily identified.

When one side or edge of the cloth is consistently darker than the other, the unevenness is caused by the pressure of the roller against the cylinder being greater at one end of the roller than at the other; if the dark (or light) band runs up the middle of the piece, it is attributable to inequalities in the lapping, or, in the case of long rollers, to their springing in the centre, where pressure cannot be applied, except by "packing" the lapping, *i.e.* by introducing strips of calico to increase its thickness in the middle. Uneven effects of a similar nature, but not so regular in appearance, are also caused by feeding fresh colour into the colour box at one point only instead of distributing it evenly from end to end; in the case of colours that froth much, or that are apt to decompose, it is most essential to replenish the box as evenly as possible, in order to keep them of the same composition, strength, and tone throughout. Unevenness is also produced by colours that are badly mixed, or which separate out in the course of working. Of these latter, pigment colours are perhaps the worst: the heavy precipitates of which they are composed are very apt to settle, especially if the printing colour is thin; and it frequently happens that, in mixtures, one constituent settles more rapidly than the others, with the result that not only is the colour weakened, but is altered in shade at the same time. The only way to prevent this settling down is to stir the colour up from time to time, both in the colour box of the machine and in the tub which contains the supply.

If a roller has been polished a good deal in one part to eradicate scratches, etc., it often happens that that particular part gives a weaker impression than the rest of the roller, owing to the engraving having been reduced in depth: or the polishing and burnishing may have been so drastic as to cause a "low place" on the roller, so that the doctor fails to clean it properly, and thus allows a smudge of colour, a sort of local scum, to be transferred to the cloth. Weak and uneven impressions are also due to the unequal depth of the engraving in different parts of the roller, and defects arising from this cause always occur at perfectly regular intervals, corresponding to the circumference of the roller.

Another factor in causing uneven printing is what is known as "lobbing" —that is, the slipping of the roller round its mandrel at every revolution. Lobbing only takes place when the roller is put on too loosely, and when its tongue or internal tab is too narrow for the groove in the mandrel, into which it ought to fit tightly, or when the mandrel itself is too small for the particular roller put upon it. In such cases the mandrel is frequently wrapped with

calico to make it fit the roller better, but this operation is not always effective, as the grinding action set up rapidly reduces the calico to small pieces, even powders it at times, and the lobbing re-commences, gradually increasing in extent until the machine has finally to be stopped, the roller taken out, and a fresh mandrel inserted.

Many other accidents are liable to happen to a piece of calico during the process of printing by machine, but the foregoing are the most usual, and to them can be traced most of the mechanical defects of work spoiled in printing. Considering how many risks have to be guarded against, and that these risks increase with the addition of every extra roller, it is really wonderful how many thousands of yards of cloth can be printed without a blemish and with so small a percentage of jobs (spoiled work), for once a piece is badly printed it is very rarely that it can be improved by any subsequent treatment short of re-bleaching and re-printing.

PART III.

PREPARATION OF THE CLOTH FOR PRINTING.

PREPARATION OF THE CLOTH FOR PRINTING.

THE operations connected with this important branch of calico-printworks routine consist of—

(*a*) Bleaching.

(*b*) Mercerising (if required).

(*c*) Winding-on, brushing, and shearing.

(*d*) Impregnation of the cloth (when necessary) with substances that are essential to the full development of the colours.

(*e*) Stentering and weft-straightening of cloth that is to be printed with certain styles of pattern.

Most of these operations are susceptible of much variation, and no one of them is carried out in exactly the same way in every works; nor is the order in which they are performed by any means invariable. Every firm adopts that process which yields the best results with its plant and under the conditions obtaining at its works, and consequently it would be impossible to describe in this work even a tithe of the numerous modifications that are employed. All that can be done, therefore, is to cite a few typical examples of the methods of bleaching, and of the preparation of cloth for printing; and as practically all methods in general use on the large scale are based upon the same principles, any variation in the details of their application will usually be found to have been adopted for the purpose of making the best possible use of existing machinery or of new plant.

Such being the case, the following processes must be regarded as a series of operations that have given good results in particular cases, and not as affording definite and unalterable data for the production of equally good results under all conditions.

(*a*) BLEACHING.

The theory of bleaching and the *rationale* of the numerous operations that are involved in its practical application have been treated exhaustively by the authors of *A Manual of Dyeing*, a work which the present volume is intended to supplement. Reference can be made to that work for scientific details respecting the composition and properties of the cotton fibre and the effect of the action of various reagents upon it, and it only remains here to deal with the process of bleaching in its relation to calico printing.

For goods intended to be dyed or printed, the cloth must not only be white (with one or two exceptions), but it must be entirely freed from foreign matters, and also from its natural impurities, which, if allowed to remain, tend to the production of stains, and in any case detract from the purity and brilliancy of the finished goods.

Apart from moisture, cotton contains about 5 per cent. of natural impurities that are more or less insoluble in water, but may be removed by successive treatment with alkalies and acids.

According to Dr Schunck, these impurities consist of fatty and waxy bodies,

colouring matter, pectic and margaric acids, and albuminous substances. In addition to these, cotton cloth contains various added impurities, such as the sizing pastes, etc., that are employed to facilitate the weaving. These consist of starch, flour, tallow, paraffin wax, soap, zinc chloride, magnesium chloride, etc., not to speak of the dust, dirt, and mineral oil from machinery that get incorporated with the fibre, and are most difficult to get rid of afterwards.

It is the object of bleaching to remove all impurities whatsoever, to leave the cloth in a condition approximating to pure cellulose, and to render it capable of absorbing, evenly and regularly, the various colouring matters and mordants that are applied to it. To this end the cloth is boiled in alkaline solutions, followed by a treatment in warm or cold acids, and finally submitted to the action of oxidising agents, which are the only substances that will remove effectually the last traces of the natural colour of the fibre.

The alkalies used are caustic soda, carbonate of soda, and milk of lime, and the boiling of the cloth with their solutions is effected in large boilers or "kiers," arranged either singly or in pairs, through which the liquor circulates continuously.

The acids employed for (*a*) decomposing the soaps formed by the alkalies with the fatty matters of the cloth, and (*b*) neutralising the excess of alkali, are, as a rule, restricted to sulphuric acid and hydrochloric acid, but acetic acid is sometimes used for special purposes, though not often, on account of its expense. The acids are applied in large machines, through which the cloth passes continuously in the rope form. In processes for bleaching cloth in the open width, the acid, and indeed all operations except boiling, are carried out in "becks," through which the cloth runs over a series of rollers fixed therein. Bleaching powder is the oxidising agent in most general use. It is applied in weak solution, and in machines similar to those used for "souring" (the treatment with acid). Between each operation the goods are well washed in a plentiful supply of water, and upon the final wash depends much of the ultimate success of the work.

The ordinary process of bleaching is carried out as follows:—

(1) **Marking and Sewing of Pieces.**—Each piece on entering the works is examined in the grey room (where all unbleached goods are stored) for faulty weaving, dirt, damages, and other defects, and after being passed, is stamped or marked, in gas tar, with distinctive letters and numbers, which not only denote its quality, source of origin, and date of arrival, but also serve as valuable aids in tracing faults and in making comparisons with previous deliveries. A suitable number of pieces are then sewn end to end and run into the singeing room. The sewing is done on machines worked by power; they are simple of construction, as such machines go, and call for no more than mention.

(2) **Singeing.**—The object of singeing is to burn off, as completely as possible, all the filaments and fine hairs that are to be found on the surface of the calico as received from the weaver. Singeing is effected in three ways: (1) plate singeing; (2) revolving-roller singeing; and (3) gas singeing.

In its most perfect form the plate singeing machine consists of two copper plates bent to a semicircular section, and arranged to form a portion of two flues leading from a coal- or coke-burning stove. By this means both plates may be heated to a glowing red heat, but, as a rule, one plate is kept considerably cooler than the other—a practice whereby great economy of fuel is secured without reducing the efficiency of the machine. The cloth passes over, and in contact with, the cooler plate first, and is thus prepared for being thoroughly singed on the hotter plate. On leaving the two red-hot plates the cloth is drawn through a steam-box or water-trough to extinguish any adhering sparks or filaments of burning cotton, and it is then ready for bleaching.

Fig. 43 represents a modern plate singeing machine in sectional elevation: fig. 44 a view of the traverse motion by means of which the wear of the plates is equalised, owing to the constant change in the position of the cloth moving over them.

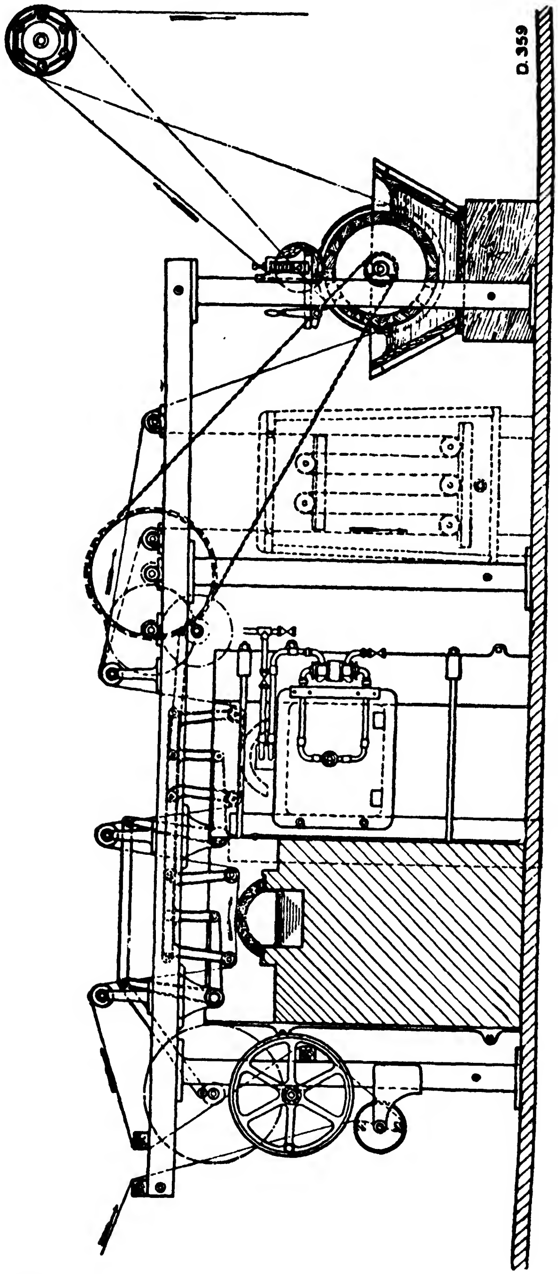


FIG. 43.—Plate singeing stove (Mather & Platt).

The chief disadvantage of plate singeing is that, owing to irregular heating or unequal wear of the plates, the singeing is apt to be uneven or "stripey," a defect which shows up very distinctly in some styles of dyeing, printing, and finishing.

This objection may be overcome almost entirely by singeing the pieces on a *revolving* roller machine. This improved machine really is a modification of plate singeing; but the goods, instead of being drawn over *fixed* red-hot plates, are passed over a hollow copper or cast-iron cylinder, through which the fire is made to pass, and which, in slowly revolving, continually brings into contact with the moving cloth a fresh part of its glowing surface. The cylinder revolves in a direction opposite to that travelled by the goods, so that the nap of the latter is raised, and thus allows more air to pass between the cylinder and the cloth, with the result that more perfect combustion is secured, and the goods singed with greater regularity. By arranging two cylinders to work side by side it is possible to singe both sides of the cloth at one operation, thus effecting a great economy of time.

Fig. 45 is a section of a revolving roller singeing machine.

In *gas singeing* the pieces are drawn over one or more powerful gas flames issuing from specially constructed burners, supplied, under pressure, with a

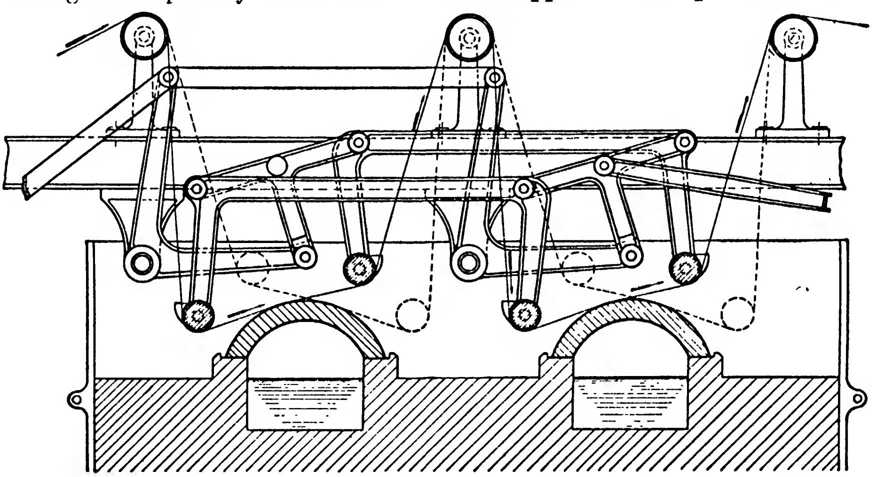


FIG. 44.—Traversing movement of plate singeing machine.

suitable mixture of air and coal gas. Exhaust hoods are frequently placed above the cloth, immediately over the flames, for the express purpose of drawing the flame through the body of the fabric, the idea being that its singeing power is thereby increased. Whatever theoretical reasons may be advanced in support of this idea, it is certain that, in practice, gas singeing machines yield better results when the flame is allowed to play freely on the under side of the cloth than when the exhaust hoods are in operation, and that, except in the case of very open fabrics, the exhaust hoods do not even draw the flame through the material, as is claimed for them. A long series of practical trials carried out on different types of gas singeing machines amply demonstrated that the only effect of the exhaust hoods was to localise the flame without adding to its intensity, as judged by the quality of the singeing it gave. As a matter of fact, the machines fitted with exhaust hoods yielded consistently poor results: the hoods were removed, and the flame allowed to spread out along the under side of the cloth, the result being that the singeing was perfectly satisfactory. The only inference to be drawn from this was, that the hoods were not merely useless, but harmful. They doubtless increase the actual temperature of the flame by concentrating its power within narrower limits, but at the same time they reduce its efficiency by restricting its sphere

of action, the increase in the temperature of the flame not being commensurate with the decrease in the area of the cloth upon which it acts at a given moment.

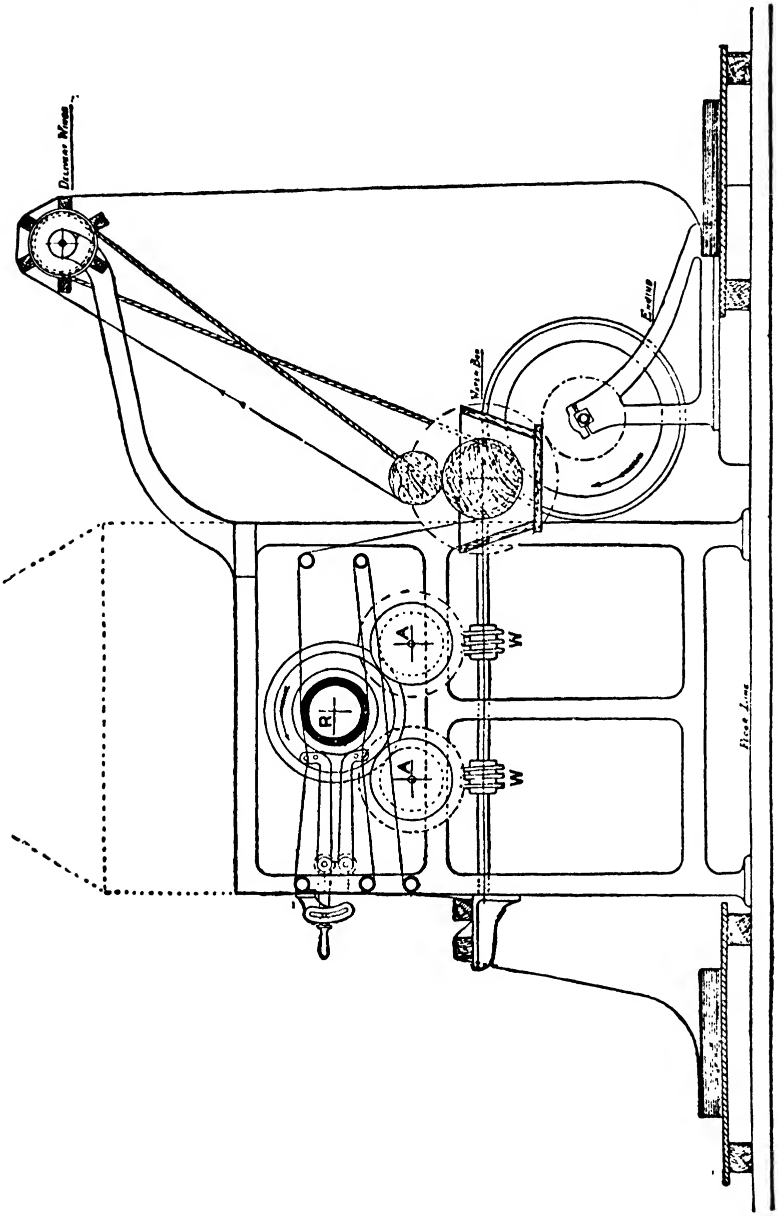


Fig. 45.—Roller singeing machine.

Of course, if the speed at which the cloth passes over the flames is reduced, it is possible to secure satisfactory singeing, but at the cost of lower production.

Fig. 46 is a diagrammatic sketch of a three-burner gas singeing machine, showing how the cloth may be arranged so as to be singed either three times on the face side, or twice on the face and once on the back, at a single operation.

The passage over two or three steam-heated drying cylinders and a revolving brush working against the cloth to raise up the flattened nap greatly facilitates the singeing, and permits of greater speeds being run.

(3) **Washing.**—After singeing, the pieces are either passed through hot water or through sulphuric acid at 3° Tw. and allowed to lie in pile overnight. In the former case—the grey wash—the impurities soluble in water are removed, and the starchy substances used in sizing are rendered soluble by the fermentation set up; the goods are also thoroughly wet out, and in the best

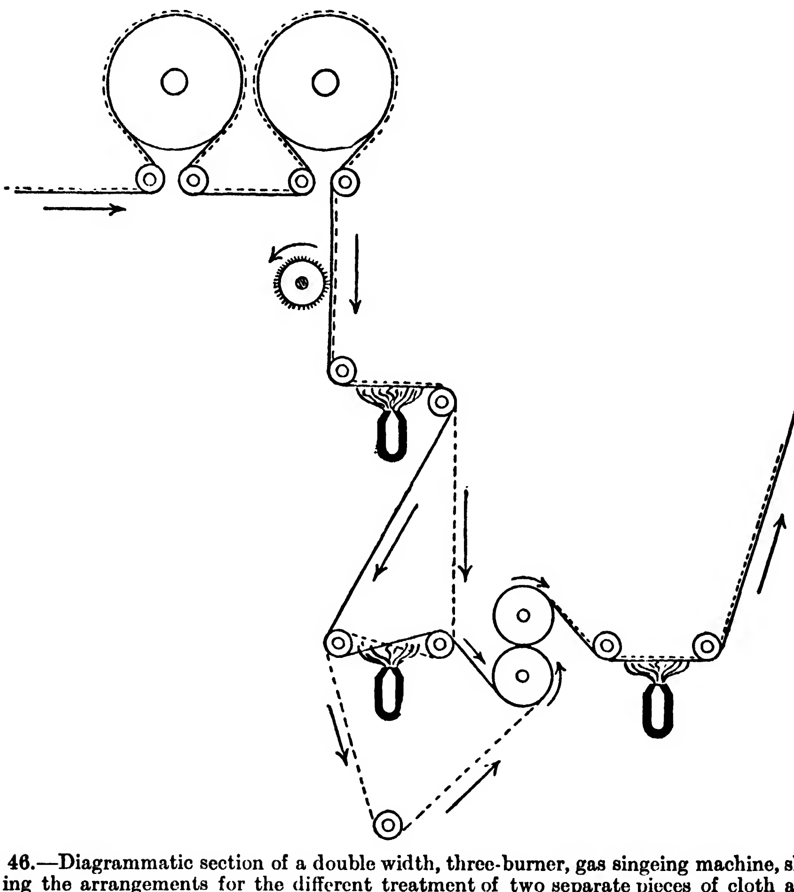


Fig. 46.—Diagrammatic section of a double width, three-burner, gas singeing machine, showing the arrangements for the different treatment of two separate pieces of cloth at the same time. The cloth travels in the direction indicated by the arrows, and the *solid black line* represents one piece singed three times on one side only, while the *dotted line* represents the other piece being singed *twice* on the face side and once on the back.

condition for being acted upon by the alkalies used in the subsequent processes. Nowadays the grey wash is usually discarded in favour of a run through weak sulphuric acid, which is found to eliminate the sizing materials much more effectually than water alone. The acid may be used either cold or at a temperature of about 60° C., and the pieces, after being passed through it, are allowed to lie from eight to twelve hours in pile, care being taken to prevent them from drying. They are then well washed in the machine shown in fig. 47, and afterwards saturated in milk of lime in a similar machine.

(4) **The Lime Boil.**—In this operation the pieces saturated in milk of lime are subjected, under pressure, to the action of boiling lime water, which circulates continuously through the material. The boiling is effected in large cylindrical boilers or kiers of wrought iron, of which various types are in use, suitable for boiling at high, low, or atmospheric pressure according to require-

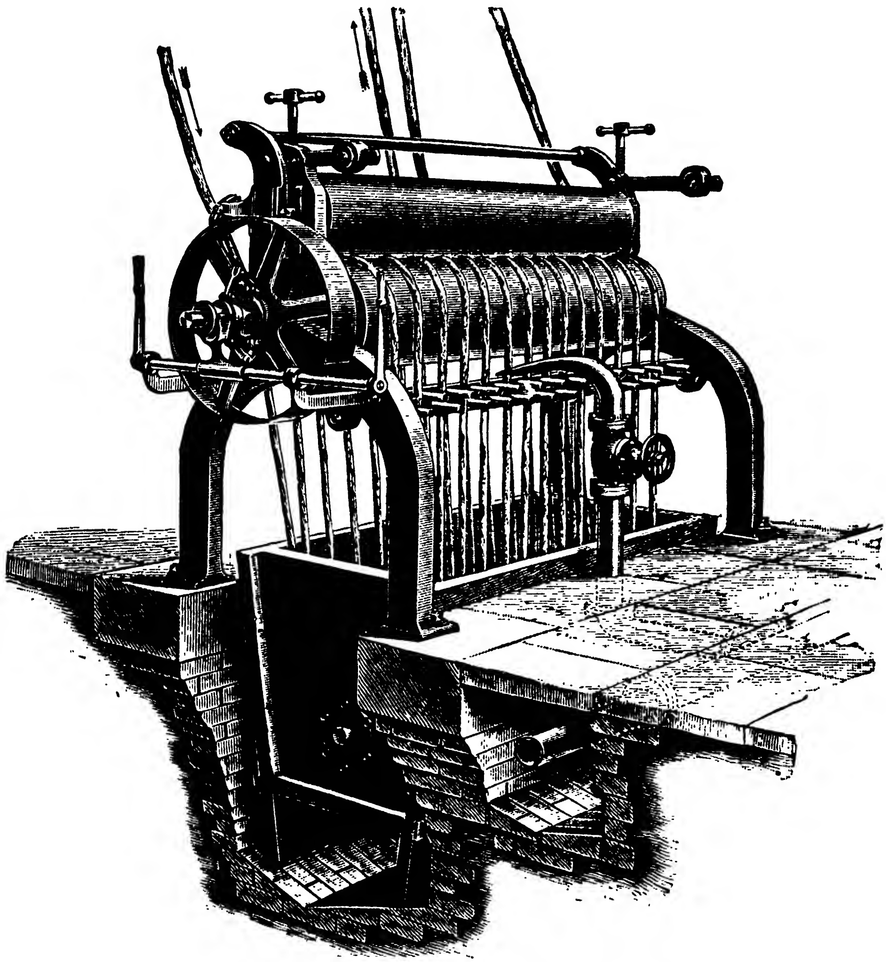


FIG. 47.—Washing (and liming) machine (Mather & Platt).

ments. The heating and circulation of the liquor in these kiers may be effected either by a steam injector or, better, by a centrifugal pump and an external multitubular heater ; or again, as in the now almost obsolete Barlow coupled kiers, by the mere pressure of the steam itself. For printing purposes the kiers in most general use are the vertical high-pressure kiers, fitted either with an injector or with pump and heater, and the " Mather patent kier," which is horizontal and possesses special features which render it particularly suitable for the bleaching of printing cloths. In the injector kier (fig. 48) the boiling liquor is maintained in constant circulation by a steam injector, which continually draws it from the bottom of the kier, forces it up a rise-pipe to the top,

and distributes it there over the cloth, through which it is drawn again to the bottom of the kier, the operations being repeated as long as the kier is working. An exactly similar sequence of operations is carried out in the vertical high-pressure kier fitted with centrifugal pump and external multitubular heater.

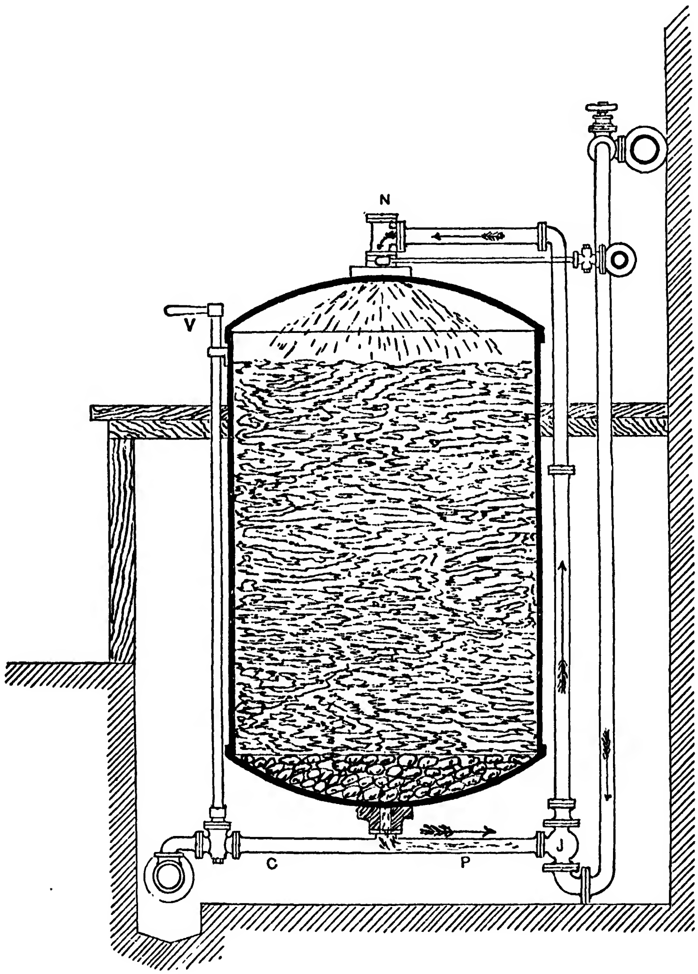


FIG. 48.—Section of injector kier.

As shown in figs. 49 and 50, the heater consists essentially of a series of tubes enclosed in an upright cylindrical casing or steam box. The tubes are let into, and pass through, the end plates of this outer casing and thus form a means of communication between two small circular chambers situated at the top and bottom of the heater respectively but otherwise independent of it. The lower of these chambers is connected with the pump, the upper with a pipe leading into the top of the kier. The kier is provided with a cast-iron false bottom, underneath which is a cavity whence the liquor is drawn by the pump and delivered through the tubes of the heater to a perforated annular pipe in the top of the kier, and so sprayed over the cloth. During its passage through the heater the liquor is raised to the required temperature by high-pressure steam

which is admitted to the outer casing (see fig. 50) and circulates round the inner tubes. The temperature is indicated by a thermometer fitted at the top of the heater. The great advantage of the multitubular heater is that no dilution of the liquor occurs from condensed steam, as is always unavoidably the case where direct steam is used, through an injector or otherwise, for heating and

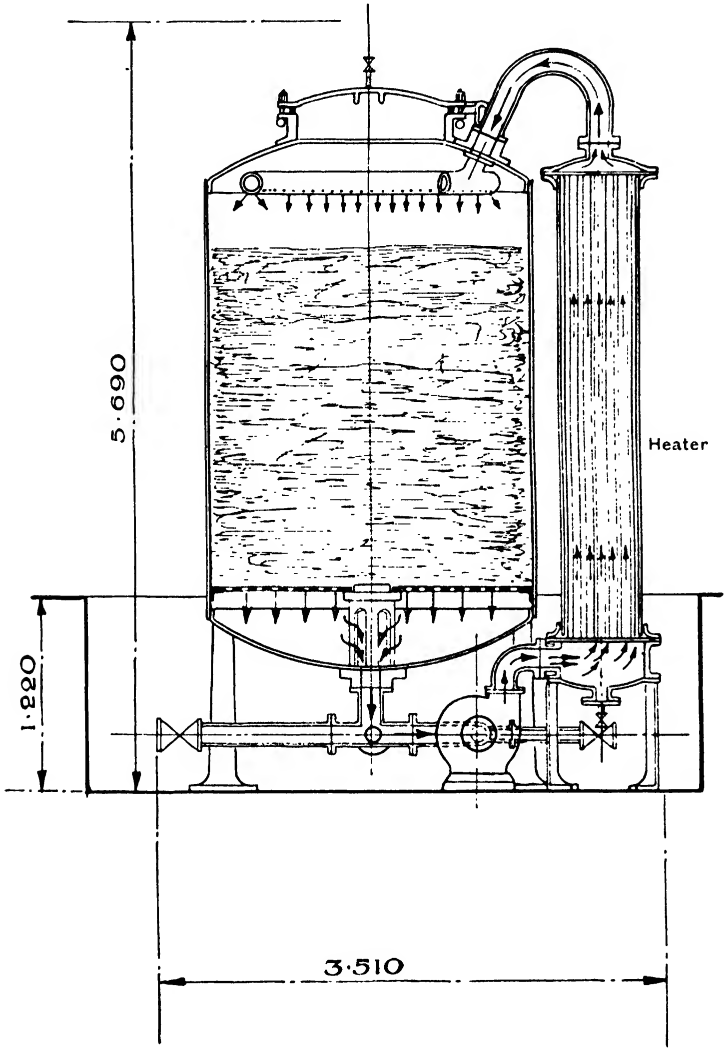


FIG. 49.—Vertical high-pressure kier with pump and multitubular heater.

circulating. All risk of oil stains is also avoided. The pump, too, provides a more regular and thorough circulation of the liquor through the cloth, and altogether the combination of pump and external multitubular heater is an improvement on older systems and allows of the process being more easily controlled.

Coupled high-pressure kiers are falling rapidly into disuse, though a few are still in operation in older English and Continental works. The bottom of each

kier is connected by a rise-pipe with the top of its neighbour, and through these pipes the liquor is forced, by steam pressure, from the bottom of one into the top of the other. When all the liquor has passed over, the steam pressure is reversed, and the alternate action takes place, the liquor passing back into the first kier. In this way two kiers full of cloth are treated with one kierful of

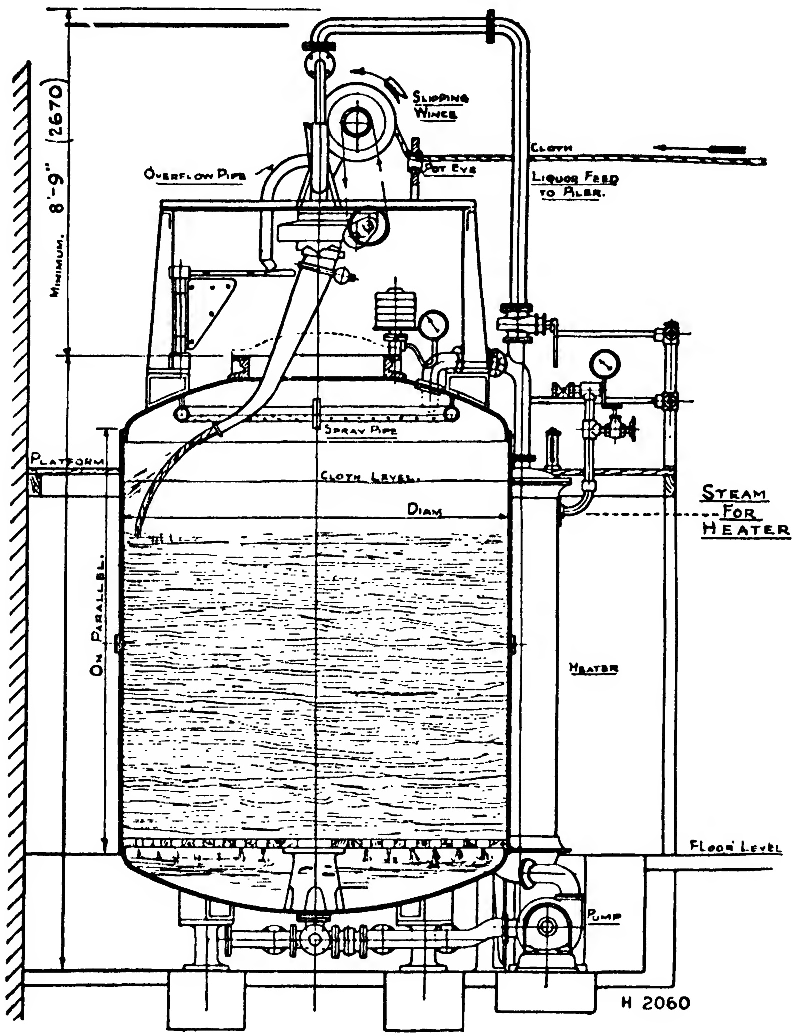


FIG. 50.—High-pressure kier with mechanical piler.

liquor, so that a good deal of time and some material is saved. Coupled kiers are dangerous to use for the lime boil, however, on account of the cloth becoming tendered by contact with the hot, dry sides of the empty kier.

Low-pressure and open kiers are also used in some works, but they are now almost obsolete except for the bleaching of cloth with coloured headings and yarn.

Whatever form of kier is employed, the cloth must be " plaited down " in it in a certain way, so as to be well packed, but at the same time not so tightly

as to impede the flow of the liquor, nor so loosely as to get displaced during the boiling. The "plaiting down" is done by boys who enter the kier by the manhole at the top and who distribute the cloth (which enters at the same place) evenly all over the kier with a stick, tramping down each layer, as it is completed, with the large wooden clogs they wear for the purpose. The many serious accidents that have befallen these boys, together with the further disadvantage of irregular and uneven piling or "plaiting down" of the cloth in the kier, due to their carelessness and to the impossibility of exercising direct supervision of their work, have led to an increasing use of *mechanical pilers.* Apart from ensuring the safety of the boys by rendering unnecessary their employment in the kiers, several other practical advantages accrue from the use of these devices. They are simple and reliable in operation, giving regular and even piling from top to bottom of the kier, with the result that the circulation of the liquor is constant and the cloth evenly penetrated throughout its entire mass; they eliminate the preliminary process of saturating with alkali, since the cloth is saturated and "plaited down" in a single operation; and the time required for filling the kier and circulating the liquor, after "plaiting down," is considerably reduced owing to the amount of hot liquor introduced by the piler. Moreover, the cloth is not distorted in any way and is also free from knots, so that it can be withdrawn from the kier without stoppages or damage. As one man can easily attend to several kiers, instead of having an operative to each rope of cloth, the working costs are reduced and there is an all-round economy. The type of piler fitted to the high-pressure kier illustrated in fig. 50 is manufactured by Messrs Mather & Platt, Ltd. It is the outcome of numerous experiments and many years of study and research on practical lines, and it may be relied upon to fulfil adequately the purposes for which it is designed.

The piler consists essentially of a feed pipe and a long oscillating trunk mounted, with its oscillating mechanism, above the kier, as shown in fig. 50. The trunk is made of galvanised sheet steel for use with the kier or of vulcanite for use with acids. In operation the cloth arrives at the kier in rope-form, and passes over a patent slipping wince, through the feed pipe and oscillating trunk into the kier; simultaneously hot liquor from the multitubular heater is also fed through the same feed and trunk pipes, and not only saturates the cloth thoroughly but also contributes to its travel forward: in fact the cloth is actually washed into the kier by the flow of the liquor. The excess of liquor runs into the kier through an overflow pipe. The actual piling by the trunk is effected by imparting to it a combined rotary and "heart-shaped" oscillatory motion by means of a belt from the slipping wince referred to above, the construction of which is such that immediately the cloth stops, the piler will also stop instantly. The turning and swinging motion of the trunk gives perfectly even piling and distributes the cloth, in regular layers, over every part of the kier. The trunk is easily detached from the mechanism when the kier is full and has to be closed for boiling. When the kier is full of cloth the manhole is closed and a quantity of lime water, sufficient to cover the cloth entirely, is run in. The amount of slaked lime used is equal to about 5 per cent. of the weight of the cloth. Steam is then turned on, and as soon as all the air is driven out, all outlets are closed and the pump is set to work. The goods are boiled six to eight hours; the lime water is then run off as rapidly as possible, and the kier filled up immediately with cold water. If this is not done, the pieces will be found to be quite rotten wherever they have come into contact with the hot kier sides, and even during the boiling they must be kept fully immersed, since if they emerge above the surface of the liquor they are certain to be tendered.

During the lime boil the fatty and oily matters contained in the cloth are

converted into insoluble lime soaps, the starch, flour, and gums are eliminated, and the remaining impurities so acted upon as to greatly facilitate their removal in the various operations through which the cloth afterwards passes. Curiously enough, the pieces appear much darker after the lime boil than in the grey state.

On leaving the kier, the cloth is well washed (in the machine shown in fig. 47) to free it from all uncombined lime and soluble matters, and is then "soured."

(5) **Souring.**—Souring consists in running the goods through sulphuric or, better, hydrochloric acid at 1° Tw. to 2° Tw. It is conducted in an ordinary washing machine (fig. 47); and although it is usually carried out in the cold, excellent results have been obtained by souring at a temperature of 60° to 70° C. with acid at about half the above strength ($\frac{3}{4}$° to 1° Tw.).

In the grey sours (the first souring) iron and other stains are removed, and the lime soaps are decomposed, leaving the free fatty acids on the fibre in such a condition as to be readily converted into soluble soda soaps in the subsequent processes.

After a thorough washing to get rid of the sours, the goods are subjected to the action of boiling soda-ash or caustic soda. Either may be used alone or a mixture of them employed: some bleachers prefer one method, others another; and, practically speaking, there is nothing to choose between them so long as the boiling is long enough. Caustic soda is certainly more energetic and does its work more quickly than soda-ash, but, for some reason, the latter is still largely used in some works, even to the total exclusion of the stronger alkali. The treatment with alkalies is known as the "lye boil."

(6) **The First Lye Boil.**—In this operation the goods are treated with either $2\frac{1}{2}$ per cent. of their weight of caustic soda or 5 per cent. of soda-ash, and, sometimes, with from 1 per cent. to 2 per cent. of resin (in the form of a liquid soap made by boiling it up with $1\frac{1}{2}$ times its weight of caustic soda). The boiling, if conducted at a pressure of 35–40 lbs. per square inch, takes from 5–7 hours, but if a lower pressure is employed the time occupied is correspondingly longer. After the first lye boil the pieces are well washed, and passed on to the second lye boil.

(7) **The Second Lye Boil** simply consists of subjecting the goods, under the same conditions of temperature and pressure, to a four hours' boil in a 2 per cent. (on the weight of cloth) solution of soda-ash, after which they are well washed again through one machine or two machines running tandem. The second lye boil is known in some parts as the "scald-off."

The function of the lye boils is to convert all fatty matter left on the fibre from the lime boil and grey sours into soluble soaps, and they also effect the complete solution of any other impurities that may be present in the grey cotton. If the goods have been insufficiently washed after the grey sours they are apt to become tendered during the first lye boil with resin. How this comes about is not well understood, but it is a well-ascertained fact that it is due, in some way, to the combined action of the resin and the acid left in the cloth. What rôle the resin soap actually plays during the first lye boil has never been satisfactorily explained, but it certainly has the effect of removing certain bodies that tend, in after processes, to produce bad whites in dyed and printed goods. Many attempts have been made to dispense with it, but it still retains a place in the list of the calico printer's "drugs"; and although beautifully white cloth can be obtained without its aid, such cloth is very apt to develop mysterious stains in dyeing or steaming, or, worse still, after being kept for some time in stock.

After the two lye boils, followed by a souring and a thoroughly good wash, the cloth may be considered, for all practical purposes, to be entirely free from

all impurities, with the exception of a little natural colouring matter that still remains. This can only be removed by "chemicking," or by a treatment with other oxidising agents.

(8) **Chemicking.**—In this operation the cloth is run through a clear solution of bleaching powder contained in a washing machine; it is then squeezed and allowed to lie in pile overnight in order to give the bleaching powder time to act. The carbonic acid of the atmosphere helps to liberate the chlorine[1] from the bleaching powder. The strength of the solution of bleaching powder used varies between ¼° and 2° Tw., according to circumstances; but it is always better to chemic twice with a weak solution than once with one that is too strong. The oxidising action of bleaching powder is very powerful, and requires to be carefully watched. For this reason the solution must be absolutely free from undissolved particles of bleaching powder, the smallest of which is quite sufficient to eat a hole in the cloth. After the chemicking, the cloth is washed, then soured in sulphuric or hydrochloric acid 1° to 2° Tw., washed again, and finally passed through a squeezer (fig. 51) and dried over steam-heated cylinders, after which it is ready for printing.

Many modifications of the foregoing process are employed in different works and for different purposes. Some firms use only caustic soda for the lye boils; others only soda-ash; and others again a mixture of the two. Occasionally, too, both lime and resin are dispensed with altogether, the cloth being merely treated with boiling alkalies (soda), acid, and bleaching powder. The latter procedure answers well enough for certain styles of printed goods and for white finishing, but in all cases where the goods are intended for "madder" dyeing it is advisable to use both lime and resin in the bleaching, not so much because they produce a better white, but because they discharge from the cloth, more cheaply and better than anything else hitherto suggested, those substances that attract colouring matter in the dye bath,—substances which are most difficult to clear from the unprinted parts of the cloth, which ought to remain a sparkling white when the goods are finished. A white, equal to the best, can easily be obtained by treating the grey cloth with bleaching powder alone, but cloth so treated is absolutely useless for printing purposes; it simply retains the bulk of its original impurities in a modified form, and these impurities give rise to unsightly and ineradicable stains and patches when the cloth, after printing, is exposed to the action of hot steam or boiling dye liquors.

As an addition to the lye boils, bisulphite of soda was recommended by H. Koechlin, and used by him at the works of Koechlin, Baumgartner & Co. at Loerrach in Alsace. The following process, based upon this suggestion, is given by E. Lauber, and is said to yield excellent results. For one ton of cloth:—

(1) Singe.
(2) Pass through sulphuric acid at 3° Tw.; allow to lie four or five hours or overnight, and then—
(3) Wash.
(4) Boil eight to ten hours at 25 lbs. pressure in—
 50 lbs. caustic soda,
 20 ,, soda-ash,
 8 ,, olive-oil soap,
 1 gal. bisulphite of soda 72° Tw.
(5) Wash well.
(6) Chemick with bleaching powder solution at about 1° Tw.
(7) Wash.
(8) Sour with sulphuric acid at 2°–3° Tw.
(9) Thoroughly wash.

[1] R. L. Taylor, *Jour. Soc. Dyers and Colourists*, April 1911.

For lighter goods, correspondingly smaller quantities are taken.

When the grey cloth contains a good deal of mineral oil the addition of aniline has been found beneficial ; spotting with a saponifiable oil, such as olive oil, also helps to remove mineral oil stains during the lye boils, and other

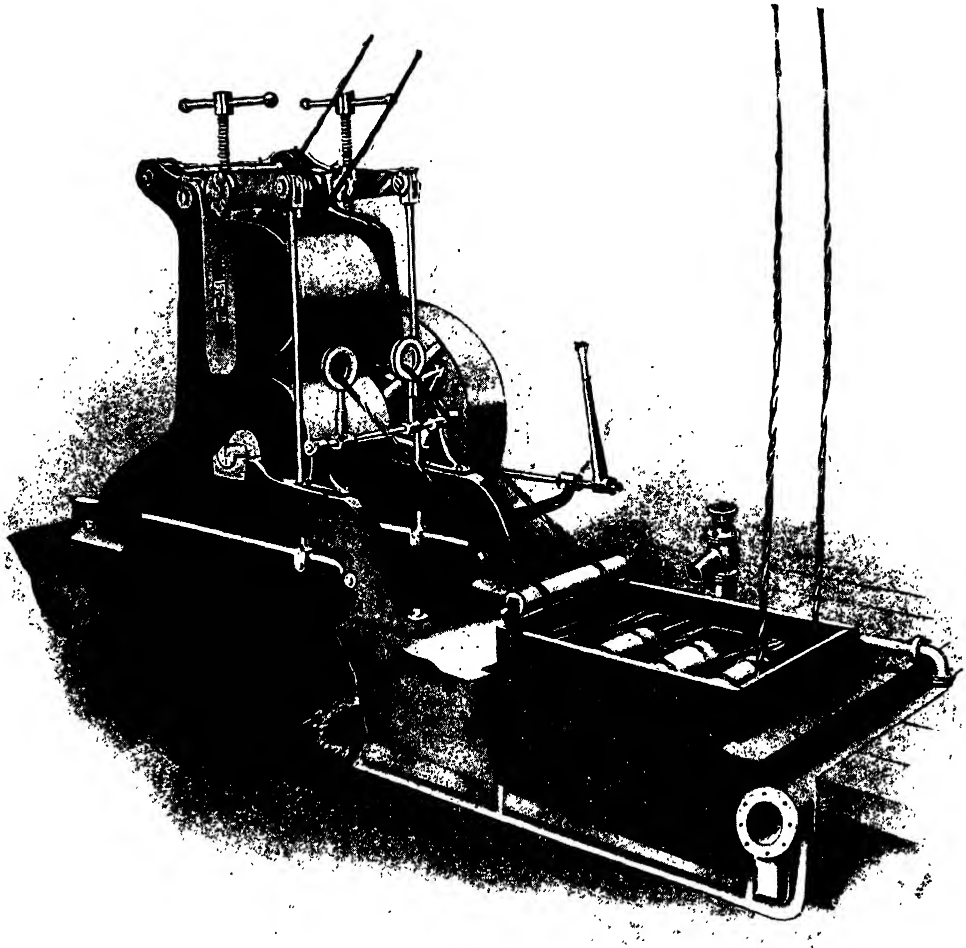


FIG. 51.—Squeezer.

substances are likewise employed for the same purpose—phenol, Turkey-red oil, and various soaps.[1]

In the Mather-Thompson process the goods, after boiling in alkalies, are passed successively through a solution of bleaching powder and an atmosphere of carbonic acid gas. This process is very little used, if at all, and cannot be said to possess any striking advantage over the older processes when they are properly carried out.

The Mather Kier.—With the introduction of the Mather patent kier, a section of which is shown in fig. 52, the process of bleaching was much shortened,

[1] No practicable and absolutely sure method of completely eliminating mineral oil stains has, as yet, been discovered.

as the operations of boiling and washing can both be performed in the kier itself. The kier consists of a wrought-iron horizontal boiler, closed at one end, and provided at the other with a heavy wedge-shaped circular door, capable of being raised or lowered mechanically and locked in position by means of a single cam and lever without requiring the adjustment of bolts.

The galvanised sheet-iron waggons into which the goods are packed for boiling are provided with open false bottoms, a perforated upright pipe in the centre and telescopic connections to the circulating pipes at the bottom of the kier. When filled with cloth (previously saturated with caustic soda) the

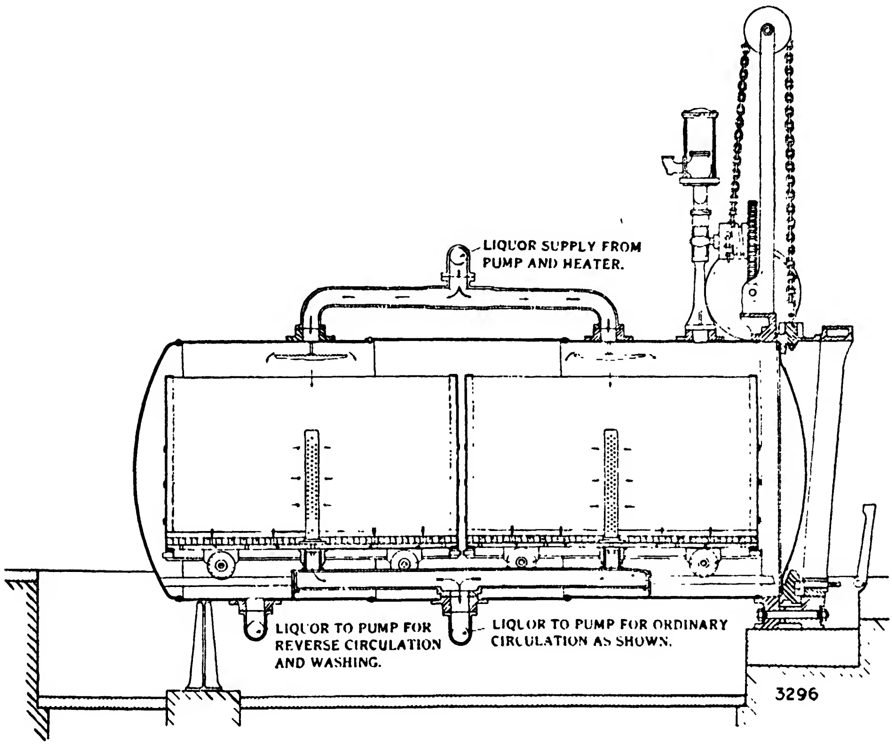


Fig. 52.—Section of the "Mather" patent kier.

waggons are run into the kier on rails laid down for the purpose: the door is then lowered into position and secured, and steam is turned on. As soon as all air in the kier is driven out, and replaced by steam, a hot solution of caustic soda is introduced, through a multitubular heater, and caused to circulate through the cloth by means of a powerful centrifugal pump which draws the liquor through the telescopic connections from beneath the false bottoms of the waggons, and showers it again *over* the cloth through distributors fixed inside the top of the kier immediately over the centre of the waggons. From the top of the waggons the liquor is drawn through the cloth, by way of the false bottoms and central perforated pipe, to underneath the waggons, whence it is again pumped up to the distributors and showered over the cloth as before, the cycle of operations being carried out continuously and at frequent intervals during the whole course of the boil. In this way the cloth is kept thoroughly saturated with boiling caustic liquor and all risk of tendering is avoided.

The circulation may be reversed if desired, *i.e.* the liquor may be percolated upwards through the cloth and allowed to flow over the sides of the waggons; and it is frequently so reversed three or four times during the course of a boil.

The kier is made in three sizes holding respectively $1\frac{1}{4}$, $2\frac{1}{2}$, and $3\frac{1}{2}$ tons of cloth, and it is constructed to work at a pressure of 40 lbs. per square inch.

Under proper conditions the "Mather" kier is capable of yielding a good ordinary bleach with only one boil. As a rule, however, two lye boils are preferable, especially for printing cloths. The following is an example of a single-boil bleach:—

(1) Singe.
(2) Wet out or pass through H_2SO_4 (2° Tw.).
(3) Wash, and saturate in caustic soda (4° Tw.).
(4) Boil four to six hours at 30–40 lbs. pressure with a sufficiency of caustic soda solution at 2° to 4° Tw., according to the kind of cotton under treatment.
(5) Wash well.
(6) Chemick at $\frac{1}{2}$° to $\frac{3}{4}$° Tw. and allow to lie several hours.
(7) Wash.
(8) Sour in sulphuric or hydrochloric acid (H_2SO_4 2° Tw.—HCl 3° Tw.).
(9) Wash well and dry.

At the present time the "Mather" kier is largely used, not merely because it reduces the time of bleaching, but also because it is very convenient, in that it can be emptied and re-filled with great rapidity, and can be used in conjunction with practically every existing process of bleaching.

The principal advantages of the "Mather" kier over other types may be summarised as follows:—

Freedom from accident to the operatives when filling the waggons, as this is done *outside* the kier.

The waggons are filled with cloth under direct supervision in the open bleach house and consequently the cloth is "plaited down" more carefully and much more evenly than is possible in the confined space of an ordinary upright kier.

Owing to the horizontal arrangement of the kier, there is necessarily a relatively small depth of cloth in the waggons. This facilitates the rapid circulation of the liquor and ensures even penetration of, and equal treatment to, every part of the contents of the kier.

The improved circulation reduces considerably the duration of the boil and results in a corresponding economy in fuel and labour.

Four waggons are supplied with each kier, so that whilst two are under treatment in the kier the other two may be emptied and refilled outside in readiness for running in. The change of waggons occupies only 10–15 minutes, so that the kier works practically continuously.

By manipulation of the valves the circulation may be reversed at will. The liquor may be drawn from the bottom of the waggons and sprayed over the top; or it may be delivered, by the pump, to the bottom of the waggons and allowed to percolate upwards through the cloth, until it flows over the sides. The circulation is often reversed several times during the boil, but for washing in the kier, after the boil, the upward circulation is by far the more effective, since any dirt or scum which may have collected on the top of the cloth in the waggons is, at once, carried away and not driven into the fabric.

The method of heating the liquor, in the original design of the "Mather" kier, by means of a closed steam coil in the bottom of the kier and by direct steam injected through internal perforated pipes, has been replaced in the present standard installation by an outside multitubular heater. The advan-

tages of this external heater are that the liquor is not diluted by condensed steam during the boil and that risk of oil stains is eliminated.

New Methods of Bleaching.—Of late years many new methods of bleaching have been proposed, in which advantage has been taken of the oxidising action of the peroxides of hydrogen and sodium, and of potassium permanganate, but, so far, none of them has replaced bleaching powder to any extent, except perhaps for special purposes with which this volume is not concerned. Sodium hypochlorite is the only oxidising agent, apart from bleaching powder, that is of any great use for bleaching in a printworks. Its great advantage is that it obviates the risk of calcium sulphate being left in the fibre if by any chance the pieces are insufficiently washed before they are soured in sulphuric acid. Notwithstanding this, it is rarely used for bleaching proper, its chief employment being for the final clearing of printed goods, and for mixing with the soap solutions used for clearing purposes in some styles.

Most of the newer systems of bleaching depend for their value upon some improvement in machinery, very few of them being based upon anything that can be considered as involving a radical departure from the old-established chemical treatment.

Of these newer systems the open-width bleaching arrangements of Tagliani & Rigamonti, Bentz & Edmeston, and Jackson & Hunt are the best known and perhaps the most efficient, though the last-named does not give a very high production. The advantage of open-width bleaching is that the surface of the cloth is disturbed as little as possible, and that the warp and weft threads suffer a minimum of distortion. When sateens and other goods with a fine close surface are bleached in the rope form, as in ordinary bleaching, their threads get twisted and their surfaces affected by the tension and pressure they are subjected to in passing through the various operations and machines. In passing between squeezing rollers the cloth gets crushed; and although the creases so formed are quite unnoticeable in the white state, they show up in all dyed goods, and many printed goods, that are afterwards finished on the Schreiner calender. As the cloth is denser where the creases or "scrimps" occur, it takes the dyestuff unevenly, and results in streakiness, to the utter ruin of the market value of the work.

A system of bleaching in use at one of the most important works on the Continent consists in performing all the operations of bleaching, except that of boiling, in the open width, and it yields eminently satisfactory results. The boiling is conducted in the rope form, in a "Mather" kier, but whilst in this state the cloth undergoes no squeezing whatsoever, and consequently all risk of abrasion to its surface and the formation of creases is avoided. On leaving the singeing machine the cloth is passed in the open width through boiling water, and then directly through a cistern containing sulphuric acid 3° Tw. at a temperature of 60° C. After standing a few hours it is washed and saturated in a series of becks furnished with top and bottom guide rollers, and indiarubber bowls at the exit end of each beck. The first beck is filled with water and the following ones with caustic soda 3°–4° Tw. The cloth passes through continuously in the full open width; as it emerges from the last beck it passes through a "pot eye" (a ring of porcelain), and, assuming the rope form, is plaited down directly in the waggons of the "Mather" kier. The lye boils are conducted in the usual way, and the cloth, on leaving the kier, and after draining a short time, is again opened out by passing over a Birch patent "scutcher." It then passes in the open width through two becks of hot water into a smaller beck filled with bleaching powder $\frac{3}{4}$°–$1\frac{1}{4}$° Tw. at a temperature of 60° C. From here it runs on to a travelling band or "creeper" of mackintosh, arranged to travel at a speed of 10 feet per minute; from the creeper it passes at once

through a beck of water, and then into a second beck containing hydrochloric acid at 2° Tw., followed by a thorough wash in a series of deep becks or cisterns, through which a constant flow of clean water is maintained. After leaving the kier the pieces pass continuously through the operations of washing, chemicking, washing, souring, and final washing, and the speed at which these several operations are carried out is equal to a production of 80 to 90 yards per minute, according to the sort of cloth under treatment.

This combination of open-width and ordinary rope bleaching is suitable for all classes of goods, from the most delicate muslins to the heaviest of shoddy flannelettes, and has been in use for some time, with conspicuous success, for all descriptions of cloth between those extremes. It is especially useful for low-grade flannelettes which, in the rope form, are excessively liable to have their selvedges torn (tech. cracked) in passing between the bowls and squeezers of washing machines, etc.

Bleaching for Turkey-Reds and Indigo Discharges is often described as a half bleach, because the cloth is only subjected to the action of boiling soda, and is not treated with bleaching powder afterwards.

Experience has demonstrated that a good, full, rich shade of Turkey-red cannot be produced on fully bleached cloth, and consequently for this style of work the goods are not bleached in the ordinary sense of the term, but are merely freed of their fatty and waxy impurities. Apart from the omission of bleaching powder, the operations are exactly as already described. The cloth is singed, grey washed, lye-boiled, soured, lye-boiled and soured again, and, finally, well washed and dried.

Although it is not usual in England to use half-bleach cloth for the chromate discharge styles on dyed Indigo, it is none the less very applicable to this purpose. The slight buffy tinge of the ground has no effect in dulling the pigment colours that are printed over it, and it is removed entirely in the white parts of the printed pattern by the oxidising action of the chromic acid liberated from the bichromate of soda or potash that is used for discharging the Indigo-dyed ground. Moreover, the Indigo dyes up a fuller shade, and more evenly, on half-bleached than on fully bleached cloth, so that it is not only more economical as regards time, labour, and material, but yields a better result. These are important considerations, well worthy of a wider recognition than they have hitherto received.

In all methods of bleaching, the greatest care must be observed at every stage to avoid the formation of oxycellulose, iron and other stains, and tendering during the lime boil, etc. The kiers must be kept well white-washed; the water must be clean; the cloth kept below the surface of the boiling liquors, or thoroughly saturated with them; the acids must not be allowed to dry on the cloth; the solutions of chemick must be filtered or settled until they are perfectly clear; they must not be allowed to come into contact with red-lead, or even flow through lead pipes; and the cloth, after chemicking, must be kept away from clean iron. The most fruitful cause of oxycellulose is the drying of pieces impregnated with bleaching-powder solution; it is also caused by their contact with bright iron, and by any lead that they may happen to contain. The slightest trace of lead is sometimes sufficient to cause serious damage; it is converted into the peroxide,[1] which is a powerful oxidising agent, by the chemick. If dirty water is used for the lye boils the top layers of the cloth in the kier act as a filter for it, and become so imbued with dirt that it is difficult to clean them in any subsequent operations. Both caustic soda and lime act detrimentally on the cloth in an atmosphere of high-pressure steam, and their solutions must therefore always be present in sufficient quantity to cover the

[1] W. H. Pennington, *Jour. Soc. Dyers and Colourists*, March 1909, p. 46.

cloth entirely during the boiling. Strong solutions of bleaching powder and undissolved particles of it convert the cotton into oxycellulose, which, if it does not render the cotton weak, at least gives rise to irregular work by attracting dyestuff unevenly.

Iron stains occur in goods that have been in contact with the bare kier sides, nails in stillages, and the iron parts of machinery. They can generally be removed by treating the cloth in a warm solution of oxalic acid or, better, potassium hydrogen fluoride, KF.HF. The effect of mineral acids dried on the fibre is too well known to require more than mention.

The defects incidental to bleaching, and their causes and cure, might be gone into at much greater length, but sufficient has now been said to show how important bleaching is to the ultimate success of a calico print, and how defects that are quite unnoticeable in the bleach-house are liable to manifest themselves in most exasperating ways in subsequent processes, and after a good deal of valuable work has been put upon the cloth.

Before leaving the subject of bleaching it may be well to note that back greys used in the printing machine are always singed before they are sent to the printer. After he has done with them they are soured, and allowed to lie *wet* in pile, to decompose the thickening and dissolve out the mordants and colouring matter that have been transferred to them from the rollers and cloth. They are then well washed and bleached in the ordinary way.

(*b*) MERCERISING.

As generally understood at the present day, " mercerising " is held to denote that treatment of woven cotton goods which imparts to them a permanent silky lustre. Strictly speaking, however, it consists in acting upon cotton with strong alkalies or other reagents which contract it, the lustre being obtained or not according to the conditions under which the fibre is treated.

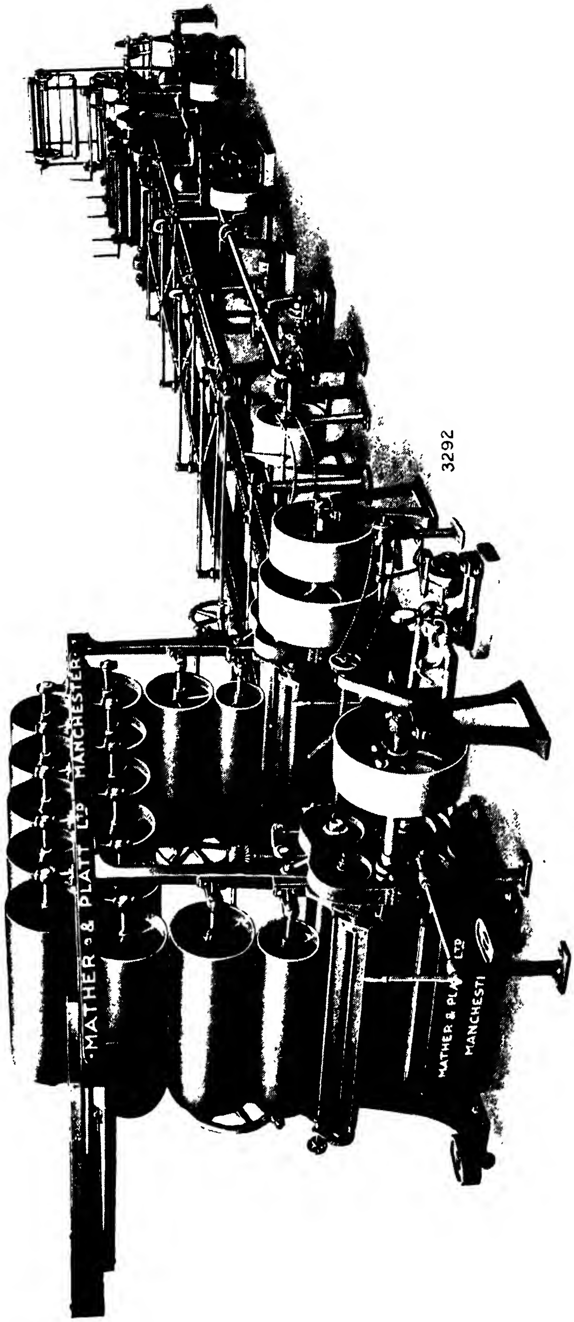
In 1844 John Mercer, of the Oakenshaw Printworks, Lancashire, made the interesting and important discovery that when cotton cloth was immersed for a short time in a strong solution of caustic soda it contracted to a considerable extent, and was so altered, both physically and chemically, that it not only possessed a much greater strength than before treatment, but also a greatly increased affinity for dyestuffs and mordants. This discovery he patented, but it never came into general use on account of the enormous shrinkage of the cloth. The process was almost forgotten when Lowe in 1889 noticed that if cotton hanks were mercerised *under tension*, to prevent their shrinkage, they attained a silky lustre in addition to the other properties resulting from the action of caustic soda, and that this lustre was practically unaffected by the various operations of dyeing. Other workers were not slow to investigate further the great possibilities of Lowe's process, and it was not long before its successful application to piece-goods became an accomplished fact.

Strong caustic soda causes the fibre to swell up, to shrink, and to become translucent and elastic—in short to become entirely changed, so that when examined under the microscope it is found to have lost completely its ordinary appearance. The fibres are no longer flat and twisted like ribbons, but round, straight, and transparent ; their walls have thickened and their central opening is closed up ; and they display no surface markings whatever. In this state the cotton, after washing, shows no lustre, but if it has been treated and washed under tension it exhibits a fine lustre similar to that of silk. The property of elasticity imparted by the caustic soda is, practically speaking, of the utmost importance, as it enables piece-goods to be " lustred " or

"mercerised" in two different ways, according to the conveniences at disposal. They may be either impregnated with soda and stretched and washed in a continuous way, or they may be "batched" after being run through caustic soda and stretched out to width and washed afterwards, care being taken neither to allow them to lie too long nor to get dry before washing. Both processes are used in printworks, the first-named being the more usual, and, all things considered, the more convenient.

If the goods are to be mercerised before bleaching, they are first singed and grey washed or soured in the ordinary manner. They are then well washed again, and either squeezed in the rope form or through a water mangle in the open width, to extract the excess of water. The latter is the better method, as it prevents the formation of crease marks. Then, without drying, they are treated with caustic soda at 50° to 60° Tw., in a padding mangle provided with two or three iron bowls, which serve to express all excess of liquor from the cloth as it passes between them. The goods may now be either batched and allowed to stand awhile, or they may be passed directly on to the "stenter" or stretching machine, upon which they are prevented from shrinking and, at the same time, washed by means of spirt pipes which deliver a constant supply of wash-water. As a rule, the first few spirt pipes are arranged to shower dilute caustic soda on the cloth so as to maintain the greater part of the washings from the cloth at a strength suitable for using in the kiers. The rest of the wash-water is employed for dissolving more caustic soda, or is concentrated in multiple-effect evaporators and utilised over again. In the case of goods mercerised in the grey state, it is not necessary to wash all the caustic soda out; all that is required is to reduce its strength below the point at which it contracts the fibre—say 10° to 15° Tw. When bleached and dried pieces are mercerised, the strength of the caustic soda may be reduced a little, but satisfactory results cannot be secured under 50° Tw., and it is therefore always advisable to work with the stronger solution. Bleached goods, after mercerising, must be soured, and then thoroughly well washed in spiral washing machines, unless, of course, they are specially intended for some process in which the presence of free alkali is not detrimental.

The simplest type of mercerising machine comprises a padding-mangle, a stenter, and a series of washing-becks provided with top and bottom rollers, over and under which the cloth runs. The stenter consists essentially of two travelling chains, the links of which consist of clips which grip the selvedges of the cloth. The distance apart of these two endless chains can be regulated, and the degree of their divergence can be adjusted at will, according as the cloth is to be stretched out rapidly or gradually. The clips are so constructed that the greater the pull of the cloth the tighter is it held; and they are also furnished with a device which not only straightens out creases at the edges of the cloth, but also prevents the clip from gripping any part of it but the selvedge. Both chains run at the same speed, and for a certain distance they diverge; after that they run parallel, or nearly so. On entering the machine the cloth impregnated with caustic soda is therefore stretched until it reaches its full width at the point where the chains commence to run parallel with each other; at this point, and whilst still held at the full stretch, it is subjected to the action of the first spirt pipe, and during its passage through the remaining length of the machine it is continuously washed by a series of perforated spirt pipes, arranged to play upon it from above and beneath. The washings are retained by cisterns situated under the machine, and planned so that the first and stronger washings are kept separate from the later and weaker ones, which are generally utilised by being pumped into the first few spirt pipes. On leaving the stenter the cloth runs directly into the hot-water washing becks,



Mercerising Range with Two Mangles.

and finally, after passing between the bowls of a mangle, into the kiers or into spiral washing machines, according as to whether it has been mercerised in the grey or the white state.

These comparatively simple mercerising ranges rendered useful service in their day, but they were somewhat unreliable in action and were often out of commission for hours at a time. The stresses set up by the contracting cloth were not always adequately provided for and frequent breakdowns occurred or the cloth was damaged. It was not uncommon for the cloth to split up the middle or to have a selvedge torn off or to slip out of the grip of the clips and, during the necessary stoppages to deal with these damages, for the rest of the cloth in the machine to be ruined by the prolonged action of the caustic mercerising liquor.

A short stoppage, or even a variation in speed, is sufficient to produce uneven mercerising, which shows up in no uncertain manner when the goods are subsequently dyed for discharge printing, etc.

Such damages as the above still occur occasionally with modern machines, but the introduction of many new features in the machines, during recent years, has reduced them to a minimum and, at the same time, has resulted in increased production, a higher degree of lustre and notable economies in the consumption of caustic soda, steam, and water.

The most lustrous effect is to be looked for when the mercerisation is performed in the cold ; and it can be always taken that the lower the temperature, the better the result. This, however, refers more especially to comparatively weak solutions of caustic soda ; for the mercerising action of concentrated solutions is so energetic that a considerable elevation of temperature makes but little difference to the lustre produced. The effects obtained by working with caustic soda at 65° Tw. between temperatures so widely separated as 0° C. and 75° C. can scarcely be distinguished from each other, whereas, on the other hand, caustic soda at from 20° to 30° Tw. will only mercerise in the cold. All the same, temperature does influence the result, and it is always advisable to work in the cold if possible.

In the mercerising of all classes of goods it is of the highest importance that the cloth be thoroughly impregnated with caustic soda ; a mere padding is not enough.

In modern practice it is customary to immerse the cloth *several* times before it passes to the stenter for stretching and washing ; and in order to attain the highest degree of even lustre these several immersions in caustic soda and the subsequent squeezings must be carried out at proper intervals, at a regular speed, and whilst the cloth is under tension so as to avoid undue shrinkage. Many types of heavy cloth contract powerfully when impregnated, and it is essential, therefore, that the machine be of strong and rigid construction to withstand the severe stresses and strains put upon it.

A modern mercerising machine fulfilling the above conditions is illustrated in Plates V. and VI. (Messrs Mather & Platt, Ltd.). It is an all-round machine, having been designed specially to deal with a wide range of goods, including plain and figured cloths of any weight or width, and bleached, scoured, or grey goods of every description suitable for mercerising.

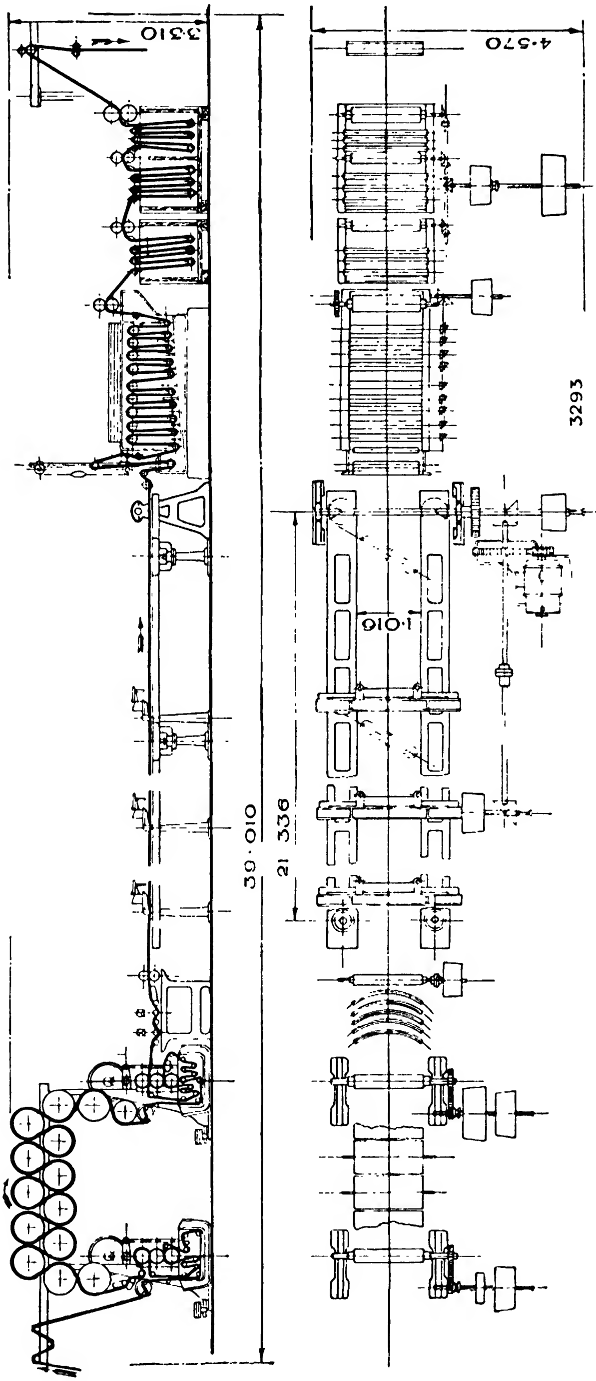
Reference to the illustrations will show that the machine is provided with two mangles, each consisting of two cast-iron bowls and one indiarubber bowl. The two iron bowls are positively driven by machine-cut gears, and the rubber bowl, which is driven by frictional contact, floats between them. By this method of driving there is no possibility of slip taking place between the rubber and iron bowls and, consequently, no danger of fraying or damaging the cloth during its passage through the mangles under heavy pressure. The

necessary pressure between the bowls is usually obtained by means of compound levers and weights, but, if required, hydraulic pressure may be provided instead. The construction of the mangle sides and of the bowl bearings allows of any or all of the bowls being removed with the greatest facility.

In the actual operation of mercerising the cloth, after passing over the guide rails in front of the first mangle, enters the caustic liquor contained in an iron trough situated under the bowls, as shown in the section on Plate VI. The rollers in the trough are arranged for two immersions of the cloth, each immersion being followed by a squeezing nip—the first squeeze (or nip) between the bottom and middle bowls, the second between the middle and top bowls. As already noted, it is desirable to keep the mercerising liquor cold, and in order to maintain a low and uniform temperature the trough is made with a surrounding cavity or jacket through which cold water or brine is circulated, or in which ice may be placed. Just before emerging from the first immersion the cloth passes over a suction pipe, which consists of a pipe with a longitudinal slot extending almost to its extremities and capable of being adjusted to suit the width of any goods under treatment. This pipe is connected with a vacuum pump and is submerged in the liquor, just below the surface, so that as the cloth passes over the slot the liquor is drawn through it, displacing the air contained in the fibre, and thus effecting a thorough impregnation. The liquor drawn through is returned to the trough by the pump, and the cloth proceeds through the first squeeze to the second immersion and squeeze. Before entering the second mangle (for third and fourth immersions) the cloth passes over a series of sheet-iron drums, the object of which is twofold, viz. (*a*) to give time for the caustic liquor to act on the fibre, and (*b*) to support the cloth in its travel between the two mangles and to prevent the curling of selvedges and also excessive shrinkage before entering the second mangle. At this point the introduction of a curved bar expander is useful; it enables the cloth to recover some of the width lost in the first mangle, and it straightens out the selvedges before the cloth comes in contact with the drums. On leaving these last the cloth passes into the second mangle, in which all the operations of the first are repeated, except that the suction pipe is omitted and a single curved bar expander is usually arranged in front of the first nip.

From the second mangle the cloth may pass directly to the stenter, but in many cases it is advantageous to introduce a five curved-bar expander between these two units of the machine, as shown in Plate VI. This type of expander assists in the impregnation by exerting a milling action on the saturated cloth and, at the same time, presents the cloth to the stenter clips partially stretched and free from creases. The maximum stretching effect of these curved-bar expanders is exerted at the centre of the cloth, and the effect diminishes progressively towards the selvedges, whereas the reverse is the case for clip stenters; hence the use of these two types of stretchers together combines the advantages of the "chainless" merceriser with the positive action of the clip stenter, and assures that the cloth shall be brought out to an exact and predetermined width and with straight selvedges.

On the stenter, in a fully stretched condition, the cloth is thoroughly washed with hot water until its caustic content is too dilute to effect any further shrinking action. The washing apparatus is an elaborate arrangement of a series of weirs, suction boxes, vacuum and circulating pumps, valves and troughs. It is highly efficient in action, giving a thoroughly searching wash, effecting great economy in the consumption of hot water, and removing the caustic soda from the cloth at a relatively high degree of concentration. The design of the weirs is such that the wash water flows over them, on to the cloth, in one smooth unbroken film of the exact width of the cloth, and thus



Mercerising Range with Two Mangles.

gives the latter an equal and efficient wash in every part. The clean and slightly alkaline wash water supply is fed into the machine from the final washing cistern (situated at the exit end of the stenter), whence it overflows into a collecting trough under the stenter. From this trough it is pumped by the first circulating pump into the first weir, over the edge of which it flows on to the upper surface of the stretched cloth. It is then drawn right through the cloth, by means of a vacuum pump, into a suction box, in contact with the under surface of the cloth, and discharged thence into a second collecting trough. From this it is pumped into a second weir and again distributed over the cloth in the same way, the operations being repeated as often as necessary by means of additional weirs and their accessory pumps and collecting troughs, the number of repetitions depending upon the length of the stenter. From the last collecting trough the wash water, now become a fairly strong solution of caustic soda, is usually pumped into a storage tank either for subsequent concentration or for immediate use in the kiers.

As only one lot of water is used for the whole of the washing process on the stenter it is evident that the weir system is extremely economical in steam and water. The heating of the wash water is obtained by closed steam coils in the collecting tanks and in the washing cistern from which supply is made to the first tank.

The cloth, on being released from the stenter clips, passes into a cast-iron cistern, fitted with a suction pipe (see before) and top and bottom rollers, where it is thoroughly washed again in hot water and finally squeezed before passing into the souring and washing becks.

The last traces of caustic soda are very difficult to remove from mercerised cloth by water alone, whether hot or cold, hence the necessity for souring; but practically the whole of it may be eliminated (before souring) if the goods are treated in a "caustic lye recovery apparatus." This apparatus consists of a closed cast-iron chamber fitted with top and bottom rollers, the former being driven. The wash water enters the chamber at the cloth delivery end, and all air is driven from the chamber by the admission of low-pressure steam, and as the cloth enters and leaves the chamber through water seals, no further air can enter. The water flows through the chamber in a direction opposite to that of the travel of the cloth, and the combined effect of steam and counter-current washing results in the almost complete removal of the last traces of caustic soda. When this apparatus is employed the waste wash water usually forms the supply for the weirs on the stenter.

The percentage and concentration of the caustic soda recovered are important factors, and by the use of an efficient system, as just described, it is possible to recover 90–95 per cent. of the original caustic soda used in the mangles.

Various other improved features in the way of stenter clips, chain rails, tension registering devices, widening screws and compensating arrangements have been incorporated in the machine, and add considerably to its convenience, easy running, and output.

The machine just described is usually designed for a maximum cloth speed of 60 yards per minute. It may be driven by any of the means in current use.

Although mercerising has long since passed the experimental stage, considerable difference of opinion still exists as to whether it is better to mercerise before or after bleaching. In some quarters it is held that cloth mercerised before bleaching is less lustrous than that mercerised in the white; and in many instances this is perfectly true. But it constitutes no argument in favour of bleaching before mercerising; for it is found that grey cloth mercerised *first* and afterwards bleached by boiling in soda-lyes, followed by the usual

chemicking, is quite as lustrous and silky in appearance as similar cloth that has been bleached *before* mercerising. The loss of lustre in mercerised grey cloth is due to the action of the *lime boil*, and can be avoided if this operation is omitted—a fact which has been proved conclusively by a long series of comparative trials on the large scale.

On grounds of economy and convenience, the stage at which the mercerisation should take place is indisputable. It should undoubtedly precede bleaching, and in many up-to-date works it does. The only feasible objection that can be made to this order of working is, that calico in its crude unbleached state is liable to absorb the caustic soda unevenly, and thus give rise to various defects in the way of stains, streaks, and irregularities of shade. In practice, however, it is found that grey cloth properly soured and washed after singeing is no more liable to contract these defects than is white cloth, and that, in point of fact, being thoroughly wet out, it allows the caustic soda to penetrate more rapidly and completely into the body of the fabric. Moreover, when cloth mercerised in the grey is once bleached, it is finished and ready for printing, etc., whereas cloth mercerised *after bleaching* requires additional souring and washing and drying at least, not to speak of still further treatment that is necessary in most cases to eradicate the stains produced by contact with the clips and other parts of the machinery. Mercerised cloth is very apt, in the white state and when wet, to contract stains from anything with which it happens to come in contact—iron or wooden rollers, stillages and waggons, etc.,—and these stains are generally so fast as to resist all efforts to remove them by washing and soaping alone. It then becomes necessary to re-chemick and sour the pieces—all of which adds to the cost of production. For this reason it is better to mercerise in the grey, when all accidental stains are removed during the ordinary course of bleaching, and the cloth enters the white room in a finished condition. Quite apart from this consideration, a notable economy is effected in time and material; the amount of caustic soda retained by the cloth is allowed for, and utilised in the lye-boils; the operations of washing, souring, and drying are reduced in number; fewer chemicals are used; and less labour is required, the cloth going through fewer processes. In addition, mercerising becomes part of the bleaching process, for the strong caustic soda employed, and the effective hot-water wash used, must perforce exercise some influence upon the natural impurities of the fibre.

Open-width bleaching is the system *par excellence* to adopt for all classes of mercerised goods; not that it gives a better white, but because it prevents the distortion of the warp and weft threads and the formation of crease marks. Good results can be, and are regularly, obtained in ordinary high-pressure, low-pressure, and " Mather " kiers, but they are more or less uncertain, owing to the fact that goods in the rope form are liable to be irregularly acted upon by the soda during the boiling. The outer folds of the rope are more thoroughly scoured by the soda than the inner, and then, again, the cloth at the bottom of the kier is pressed into a compact mass by the weight above it, and this obstructs the regular percolation of the circulating liquor, so that the lower layers of cloth are subjected to a less searching scouring action than the upper, with the result that the cloth is irregularly treated, and thus develops stains and patches in subsequent operations. Streaks running in the direction of the warp are of everyday occurrence in sateen, twill, and broché cloth that has been bleached in the rope form, but they rarely appear in that bleached in the open width. Such defects are due, in the main, to the folds of cloth being crushed into each other in passing between the squeezer bowls of washing, souring, and chemicking machines, which abrades the cloth and displaces its threads; they may also be caused by the weight of cloth in the kiers. Whatever their origin, they are

serious disadvantages in any cloth that relies for the greater part of its value upon its lustre. In plain goods the distortion of the threads is scarcely noticeable, but in mercerised sateens and the like, especially if they are finished on the Schreiner calender, every such defect manifests itself distinctly, and detracts considerably from the value of the goods. Open-width bleaching, therefore, is to be preferred for mercerised goods whenever possible, although, with care, satisfactory results can be obtained from ordinary kiers.

Within recent years Edmeston and Reuss have patented a process of combined mercerising and lye boiling, the cloth running directly from the mercerising machine into the well-known Bentz continuous kier. It is an attractive process, and, in *experienced* hands, might be expected to yield good results at a minimum cost for labour and material. In common with all long, continuous processes, however, it has the disadvantage that if the cloth happens to break, or any part of the machinery to get out of order, the whole arrangement comes to a standstill, and a considerable amount of time is required to adjust matters and get the machine running again. As a rule, the simpler and shorter a process is, the more likely is it to work with regularity.

(c) SHEARING, BRUSHING, AND WINDING-ON.

Before the bleached calico can be placed in the printing machine it requires to be wound into a compact " batch " or roll on a hollow wooden or iron roller,

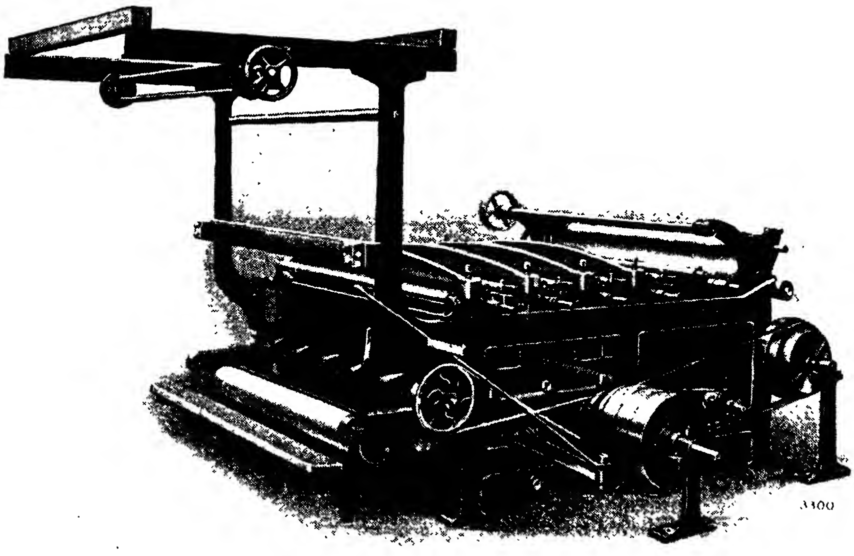


FIG. 53.—Four-cutter shearing machine.

through the central opening of which an iron spindle is passed for the purpose of supporting it in the machine. In addition to winding-on, the cloth usually requires shearing to remove the nap from its surface, and then a thorough brushing to clear it from all adhering loose threads and cotton down or fluff, which would, of course, lead to snappers in printing if allowed to remain. The brushing, shearing, and winding-on are all performed on one machine (fig. 53), which is provided with helical cutters, revolving at a high speed,

revolving brushes, and a batching arrangement. In fig. 54 is shown, in section, the assembly of a six-bladed helical cutter (A), three guide rollers (B, B, B), ledger blade (C), and faller beam (D), all of which are adjustable. The cutter revolves at a high speed against the ledger blade and shears the nap off the cloth in much the same way that a lawn mower cuts grass. The cloth travels through the machine in the direction of the arrow and its position in relation to the cutter is so adjusted by the faller beam (D) and guide rail (E) that it impinges on the cutter exactly at the point where the latter meets the ledger blade (C). This adjustment requires to be made with great nicety, otherwise the cloth is cut to pieces.

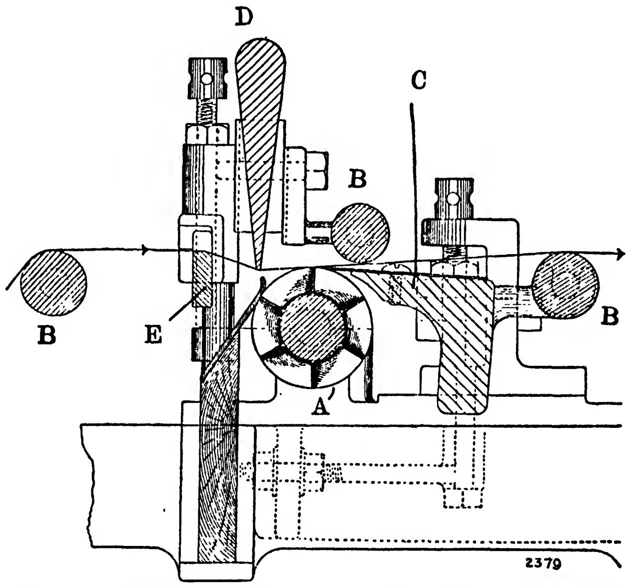


Fig. 54.—Section through a six-bladed helical cutter, ledger blade, and faller beam.

(*d*) STENTERING AND WEFT-STRAIGHTENING.

In certain classes of work it is necessary to damp the cloth and dry it over a stentering machine fitted with a weft-straightening arrangement and a batching apparatus. Amongst the styles that require the cloth to be treated in this way the following may be regarded as the most important:—Fancy woven goods in which the woven pattern and the printed pattern must be quite straight (example: transverse printed stripes on vertical woven stripes, or *vice versa*, forming a check); large printed spots on geometrical woven designs; bands of pattern printed between woven stripes; check patterns printed on any kind of cloth; and also such things as madder-dyed handkerchiefs which have to be filled in afterwards by hand block printing. If any of these styles is printed on crooked cloth to start with, the printed design will be pulled out of shape when the cloth is subsequently straightened in the finishing processes. Either the printed pattern must be sacrificed or the cloth pattern must be left crooked; it is impossible to have both right if the cloth is not properly prepared at the outset. Printed on fancy woven fabrics that are not straightened after bleaching, large spots and designs based on the circle become distorted when the cloth is afterwards straightened; squares take the form of irregular diamonds; straight lines become undulating; checks,

instead of being regular, float about in all sorts of directions ; and, in short, the whole work is bad. It is an important point, therefore, to consider carefully the style of design for which the cloth is intended, and act accordingly.

Drying to width over a stretching machine or stenter is also essential in the cases of patterns that are engraved for a certain width of cloth or with a border at each side. Any trusting to luck to provide the proper width in these cases usually results in one or other of the borders running over the edge of the selvedge, and being printed on the back grey or blanket.

(*e*) PREPARATION OF THE CLOTH WITH "PREPARES."

"Preparing" is a technical term used to denote the impregnation of the cloth with various chemical preparations that are essential to the brightening of the printed colours, or to their formation and full development on the fibre. The composition of these various "prepares" will be dealt with farther on in connection with the particular styles with which they are associated ; but as their application to the cloth takes place before printing, it falls within the scope of the present chapter.

The preparing of cloth is usually conducted in a padding mangle by the process known as slop padding. The padding mangle or foulard (see fig. 55) consists of two squeezing bowls—the upper one (A) of iron covered with india-rubber, and the lower one (B) of brass—arranged over a box or beck (C), fitted with guide rollers of wood provided with brass journals and working in brass bearings. The box ought to be of wood, and capable of containing from

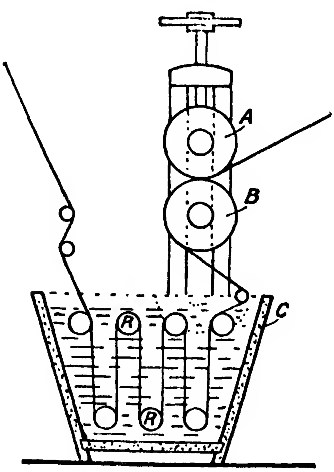


FIG. 55.—Padding mangle.

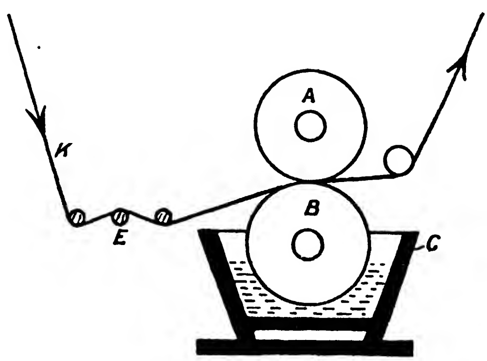


FIG. 56.—Another type of padding mangle.

15 to 30 gallons of liquor, according to the work in hand. The guide rollers R, R are arranged so as to allow of the cloth passing five or six times through the liquor before going through the squeezer bowls.

On emerging from the padding mangle, the goods run directly either on to a cylinder drying machine or through a hot-air drying apparatus, after which they are wound on in the usual way, and are then ready for printing.

In many cases the squeezer bowls are made of wood, the bottom one being wrapped with several folds of calico ; and for special styles and fancy woven fabrics the goods are treated either wholly or in part on stentering machines, for reasons already given.

A special form of padding mangle is used for cloth which has been printed in certain reserve or resist colours, and which has afterwards to be either prepared or dyed-up in the padding mangle. In such cases, if the printed cloth were passed through the liquor contained in the box of an ordinary padding mangle, the printed portions would be dissolved off, and either spoil the padding liquor or run into the surrounding parts of the cloth. To avoid this, the bottom squeezer bowl is arranged to dip into the padding liquor, and the cloth is passed straight through the " nip " (that is, between the bowls), and then dried before the solvent action of the liquor can take effect. The bottom bowl is wrapped with calico, and carries the liquor up to the cloth in much the same way that a furnisher does to an engraved roller in a printing machine. Fig. 56 illustrates the principle of this method of working. In this illustration, A indicates the indiarubber bowl ; B, brass bowl ; C, padding box ; E, tension rails, corrugated to open the cloth out ; and K, the cloth.

Padding straight through the " nip," or slop padding, is not, strictly speaking, a preparation of the cloth for printing, but as preparing is used for purposes other than printing, it may as well be mentioned here as elsewhere ; goods dyed before printing will be dealt with under Discharge Styles.

PART IV.

PREPARATION OF COLOURS FOR PRINTING.

PREPARATION OF COLOURS FOR PRINTING.

The preparation of the colours for calico printing, and of such of their constituents as are made in the works, is at the present time more of a science than an art, and demands for its proper carrying out a large amount of chemical knowledge. It is useless nowadays for a colour mixer to attempt to keep abreast of the times unless he possesses a sufficient knowledge of the chemistry of his business to enable him to get his effects without referring to his grandfather's "receipt book," and without spending a vast amount of time in making trials, trusting to a lucky fluke to yield him the effect he is groping for. Although many old colours, that were applied successfully to calico in the early days of the industry, were the outcome of scientific research on the part of chemists, the greatest number of old-time colour mixers worked on the principle of trying "a bit of this and a bit of that"; and if success occasionally crowned their unaided efforts, it was usually a long time in coming, and when it did arrive it was due rather to chance than to any systematic method of working. With the introduction of coal-tar colours the importance of the "rule of thumb" colour mixer and of his mysterious secrets began to dwindle, and has continued to do so, until now he is expected (if he still exists) to do little more than to supervise routine work. The chemist has taken his place in all that relates to the introduction of new styles, and in many cases, more especially on the Continent, the colour mixer himself is a trained chemist. In the old days practical experience counted before everything—and indeed it is no less valuable to-day, for there are still many "tips" and "knacks" that no amount of university training can impart; but nowadays a printworks run on unscientific lines has absolutely no chance of equalling the best work of its up-to-date competitors who employ a staff of specially trained chemists. Experience is necessary, but it must be supplemented by a thorough knowledge of the principles upon which modern calico printing is based. Many substances, such as Paranitraniline red or Aniline black, would never have been brought within the range of practicability save by the investigations of chemists; they afford little or no indication of their tinctorial powers; and if, in many cases, these powers were hit upon accidentally, they were at least discovered during the course of scientific work that would never have suggested itself to the mind of, or been undertaken by, the purely "practical man."

Quite apart from all questions of discovery, the mere application of many modern colouring matters demands the supervision of a chemist; and indeed all the operations relating to calico printing ought to be under scientific control. The conditions under which a colour is prepared, the proportions of its ingredients, the order in which they are added, and other points, all affect the result. Again, on the other hand, the result may be perfectly satisfactory, but obtained at too great a cost. In all these cases the services of a chemist are essential, if only on grounds of economy, not to speak of the improved quality of the work turned out.

The actual composition of the various colour pastes used in calico printing

will be dealt with in another part of this volume under the heading of "Styles of Printing," the object of the present chapter being merely to treat, in a general way, of the more important means, methods, and materials employed for the purpose of thickening solutions, etc., of colouring matters and mordants. The substances used for this purpose may be divided into two distinct classes: (1) those which are used solely as thickening agents, and are afterwards removed, as completely as possible, from the cloth; and (2) those which are thickening agents and fixing agents combined, and are allowed to remain on the cloth, forming, as they do, an integral part of the finished colour. The function of a thickening belonging to the first class is simply to act (*a*) as a vehicle for carrying the colour to the cloth, and (*b*) as a preventive against its spreading, by capillary attraction, beyond the limits of its allotted space in the design. It ought, therefore, to possess no affinity for the colour or the mordant with which it is mixed, otherwise, on washing it out of the cloth, a good deal of the colour would be removed along with it.

The following are the thickening materials in most general use:—

1*st Class*: Starch, flour, gum tragacanth or "dragon," gum Senegal, gum arabic, Karaya gum, tragasol, dextrin and other artificial British gums—with or without the addition of china clay, etc.

2*nd Class*: Albumen, casein, lactarine, and glue.

Other materials, such as linseed mucilage and Iceland moss, etc., are also sometimes employed for special purposes, but they are not essential to any style of work, and can be replaced in all cases by one or other of the many natural and artificial gums.

Starch is a substance very widely diffused throughout the vegetable kingdom. It is found in almost every plant, and occurs in the form of minute granules in the seeds of various cereals, in the bulbs and tubers of many plants, and also in the bark and pith of many trees. It is an important article of manufacture, and, on the large scale, it is obtained chiefly from wheat, maize, potatoes, and rice. Wheat, maize, and rice are ground up with cold water and a little caustic soda, which dissolves out the gluten and facilitates the separation of the starch. The milky liquor is well stirred up, and then run through coarse sieves (to separate any fibrous matter that may be present) and allowed to settle. The clear water is then drawn off, and the deposited starch well washed several times with cold water, again allowed to settle, and finally dried in shallow trays or boxes at a gentle heat. When perfectly dry the cakes break up into thousands of the small irregular masses so characteristic of starch, and the starch is either sold in this form or is ground to powder. Potatoes contain practically no gluten, and the starch is simply washed out of them with cold water. The potatoes are pulped, placed on sieves, and washed in a stream of water. The milky liquid is then allowed to settle, the deposited starch washed by decantation, and then dried as above.

Starch $(C_6H_{10}O_5)_n$ is a carbohydrate, insoluble in cold water and alcohol. With boiling water the granules swell up and burst, forming a smooth, homogeneous, gelatinous mass, in which form it is used for stiffening printed goods and for laundry purposes; but the starch paste obtained in this way is not really a solution of starch. When, however, starch is heated under pressure with water at a temperature of 150° C. it goes into solution, and the solution, on cooling, deposits what is known as "soluble starch," a product largely employed for finishing all kinds of cotton fabrics. Soluble starch dissolves sparingly in cold water, but is completely soluble at 70° C. and upwards. Other methods of making this modified form of starch are practised, but they are not of interest to the colour mixer on account of the impossibility of thickening

printing colours with soluble starch. When boiled with very dilute sulphuric or hydrochloric acids, starch is converted into dextrin and loses a good deal of its thickening power; indeed most ordinary acids, except acetic acid, have the effect of thinning starch paste, and consequently it is unsuitable for use in strongly acid resists and reserves, which consist for the most part of citric, tartaric, and oxalic acids in combination with bisulphate of soda. It *is* used for these resists and reserves, but British gum is usually preferred.

With caustic soda, starch paste forms a stiff, white, transparent jelly, known as *apparatine*. This finds a limited employment in finishing operations; but, so far, it has not been used to any extent for printing colours, although, when neutralised with hydrochloric acid, it has been tried as a substitute for gum tragacanth.

Diastase converts starch into maltose and dextrin without injury to the fabrics upon which it is printed, and without affecting the colours, and is used occasionally to assist in removing starch thickenings from cloth that is required to be specially soft in feel.

All starch pastes give a characteristic dark blue coloration with iodine, but the colour is so intense that if the various starches do give slightly different tones of blue it is impossible to distinguish them sufficiently well to use this reaction as a test for any particular starch. For this the microscope must be used: each starch has a differently shaped granule, and these can be easily distinguished from each other under a moderate power.

The most important starches to the calico-printer are the following:—

(1) Wheat Starch.—Wheat starch is the most largely used of all the thickening agents employed in textile printing. It is cheap, is not easily acted upon by colours and mordants, is useful for a greater variety of purposes than any other thickening, and gives a good, sound, workable paste, which keeps well, and may be used either alone or mixed in any proportion with other suitable thickenings as required.

As a general rule, it may be taken that the greater the weight of thickening material contained by a given colour, the lighter will be the shade it ultimately yields; and, conversely, the greater the weight or quantity of water, the deeper will be the shade. Starch paste containing 12½ per cent. of wheat starch forms a more or less aqueous thickening, which, despite its fairly thick consistency, allows the colour to penetrate well into the body of the cloth, and thus yields shades that are fuller and more opaque in quality than those yielded by any of the gums (except tragacanth), which only thicken from one to three times their own weight of water.

Starch paste prepared with water alone is somewhat too sticky to work well in machine printing; it adheres tenaciously to the rollers, and if at all thick it frequently escapes past the cleaning doctor, unless great weight is put upon the latter—a practice which tends to wear down its edge rapidly, and is, moreover, unnecessary with properly prepared colour. It also sets into a stiff mass when cold and after standing a while, and requires warming up again before it can be used. In order to avoid these disadvantages, it is rendered softer or more emollient by being boiled with a small quantity of some vegetable oil, which brings about the desired end without reducing the consistency of the paste, and makes it possible to work very thick colours without difficulty. The oils used are generally either olive, rape-seed, cotton-seed, or castor, and the quantity added varies between 25 and 50 per cent. of the weight of starch used, according to the thickness of the colour and the purpose for which it is intended.

In making starch paste, the starch is first of all stirred up with cold water into a smooth, creamy paste; the oil is then added, and the whole boiled until

the thickened mass begins to thin again. At this point the boiling is stopped and the paste cooled down. To obtain the best results, the paste should be stirred continuously during the whole of the time that the boiling and cooling are in progress. When dyewood extracts and solutions of dyestuffs are thickened directly with starch, the same procedure is adopted; the starch is beaten up with water, and the dyestuffs are added, either hot or cold. The mixture is then boiled and cooled, and before removal from the pan, the necessary mordants are added and well stirred in. Acetic and other organic acids are largely employed for dissolving dyestuffs, but their presence makes no difference to the method of working. The thickness of starch paste varies according to the style of work in hand and the strength or depth of the engraving of the rollers. For most work a paste containing from 12 to 15 per cent. of starch is quite enough; but for coarse engraving, from which a sharply defined impression is desired, and for all crisp, delicate designs, not too lightly engraved, the quantity of starch may rise to 20 per cent.; on the other hand, for padding, that is, printing a flat colour over the whole surface of the cloth, the weight of starch in the paste rarely exceeds 6 or 8 per cent., as otherwise the printing is apt to appear thin or bare.

A good wheat starch ought not to contain more than 15 per cent. of moisture, nor leave more than 0·5 per cent. of ash after incineration. In other respects its suitability for calico printing can only be determined by a practical trial. A sample of the starch is taken and made into a paste; its whiteness and thickness are then noted and compared with a sample of the standard starch in use, boiled up at the same time under exactly the same conditions. A pale Alizarin pink and a pale Methylene blue are then made up from both starches, and printed, steamed, and washed together; the shades they give are compared, when the brighter colours denote the better starch. A portion of each of the two pastes is now allowed to stand a few days, and then tested with litmus for acidity, and further examined to see whether it has retained its original consistency, or whether it has broken up into a rough, curdy-looking mass of lumps of paste, floating about in a watery medium. The whiter and thicker the paste obtained from a given weight of starch, the brighter the colours it yields; and the longer the paste will keep without turning sour and without breaking up into lumps, the better is the starch for all purposes connected with the thickening of printing colours.

Wheat starch is almost always used for thickening dark shades of all classes of colouring matters; it is not better than gum tragacanth, but is much cheaper and quite as good for all styles in which the cloth is not required to be particularly soft after finishing. It certainly does impart a somewhat harsh feel to the cloth when printed in large, heavy masses, such as occur in cretonne designs; but in practice this defect is more or less overcome by mixing the starch thickening with various proportions of gum tragacanth thickening, which, although it may be quite as thick as starch paste, contains a very large percentage (95 per cent.) of water, and consequently does not stiffen the cloth to anything like the same extent that starch does. Fine patterns in fast colours are almost invariably printed with wheat-starch thickenings, unless the colours used are pigments, Indigo and other alkaline colours, or mordants for madder dyeing.

Maize Starch alone finds but limited application in textile printing. Its chief use is for thickening aluminate of soda (alkaline mordant), and occasionally it is mixed with British gum for Indigo and Sulphide printing colours.

Used alone maize starch is unsuitable for thickening stock colours, as it deteriorates rapidly on keeping, breaking up into a rough curdy state with separation of water. An addition of 20–25 per cent. of its weight of tapioca

flour improves the stability of the paste considerably, and enables maize starch to be used with advantage in many ordinary steam colours, especially such as are consumed in large quantities, which are, of necessity, made at frequent intervals. It cannot replace wheat starch satisfactorily in every instance, *e.g.* logwood black, but where the above mixture is applicable its lower cost is a recommendation.

RICE STARCH forms an unstable paste, and is not used for anything but finishing or stiffening printed goods, for which purpose it is prepared as required.

POTATO STARCH is also restricted to finishing operations, and is of no use whatever for thickening printing colours which have to be kept for any length of time.

FLOUR.—In addition to the starch it contains, wheat flour also contains a nitrogenous body—gluten—the presence of which renders it unsuitable for use with many modern dyestuffs and their mordants. It finds its most important application in thickening the acetates of alumina and iron, which are still largely used for the production of Madder reds, chocolates, and purples, a style that was formerly in much greater demand than at present, but is still produced in large quantities whenever the best and fastest work is required. For this purpose wheat flour is eminently adapted; it is a powerful thickener, forming a soft, full paste, which allows the mordants to penetrate well into the cloth, and yields, on dyeing, dark, rich colours that are remarkable for their evenness and bloom. With the Azoic colours (diazotised Paranitraniline, etc.), wheat flour gives darker shades than most other thickenings, and possesses the further advantage of producing the most stable printing pastes, although no azo colours will remain in good condition for many hours, except in the coldest weather. Flour is frequently mixed with starch or gum tragacanth, according to the quality of paste required for a given style; it is very rarely used alone nowadays. The testing of wheat flour is carried out in exactly the same way as the testing of starch, and its technical value depends upon practically the same properties. The colour-printing trials are, of course, made with the colours for which it is best adapted, but in other respects the same good qualities are to be sought in flour as in starch, namely, whiteness, thickness, and stability.

GUM TRAGACANTH.—Gum tragacanth or "gum dragon" is a natural gum obtained from a genus of leguminous plants, of which the most important is the *Astragalus gummifer*. Tragacanth comes into the market in the form of dry, horny scales or leaves, which vary in colour from white to deep yellow, and are more or less translucent according to their source of origin. The best and most expensive quality of gum tragacanth is white, very translucent, and free from sand, woody fibre, and dirt; it ought to dissolve completely in water, and form a thick, smooth paste with at least twenty times its weight of water. When boiled, the mucilage becomes thinner, but smoother; and if boiled under pressure, the solution becomes very thin. In common with all natural gums, tragacanth varies in its behaviour towards tannic acid, metallic salts, and alkalies, the best sort for calico printing being that which does not become gelatinous with the above substances. Most qualities will mix fairly well with dilute alkalies, but, curiously enough, the best quality is converted into a ropy mass by strong solutions of caustic soda, whereas the cheaper and poorer quality, yellow in colour, and containing a comparatively high percentage of foreign matter, can in many cases be mixed perfectly with soda sufficiently strong to discharge tannin mordant. It varies considerably, however, in this respect, no two seasons' deliveries being quite alike in their behaviour towards alkalies.

Gum tragacanth is chiefly used, either alone or in combination with a little starch, for printing dark, heavy blotches, and for this purpose it is unexcelled, as it is easily removed from the cloth in washing, and leaves it almost, if not quite, as soft as it was before printing. It is also extensively employed for pale blotches or grounds for delaine printing, and for all first-class work in which softness of feel is a desideratum. It is mixed with albumen in the making of pigment printing colours, and enters into a good many of the dye liquors and prepares that are padded on the mangle. In the latter case it tends to equalise the absorption of the liquors by the cloth and ensures level padding. The tragacanth thickening or mucilage used for ordinary blotch printing contains from 6 to 8 ozs. of gum per gallon (say 4 to 5 per cent.); stronger mucilages are made (7½ to 10 per cent.), but they are employed solely for adjusting the thickness of colours that are too thin, and for mixing with solutions of dyestuffs, etc., in order to bring them up to the proper consistency for printing.

In making tragacanth thickening, the requisite quantity of gum is soaked in water until it has swollen up into a thick paste; it is then placed in a jacketed, steam-heated pan, fitted with mechanical agitators, and boiled and stirred until perfectly homogeneous, after which it is cooled and strained ready for use.

Gum Senegal and Gum arabic.—Both these gums (including gum gedda, etc.) are exudations from various species of *Acacia*, and come from various parts of the world. They occur in commerce in the form of rounded or irregularly shaped pieces, varying in size from that of a pea to that of a chestnut, and in colour from a very pale yellow to a deep brownish-red. They are nearly odourless, and of an insipid or slightly sweet taste. They are complex in composition and constitution, but they are composed in the main of one or all of the three bodies, arabin, cerasin, and bassorin, together with a little lime, potash, and magnesia.

The best qualities of gum Senegal are obtained from *Acacia Senegal*, a tree which forms dense forests in Nubia, Senegambia, and Kordofan. The various sorts of gums that come from India, Australia, and the Cape are of inferior quality; they all contain a comparatively high percentage of bassorin, which is insoluble in water, merely swelling up into a sticky, gelatinous mass, which reacts unfavourably with the various components of most printing colours.

In choosing a gum of the Senegal class for printing purposes preference ought to be given to that sample which is most easily soluble in water, gives the clearest and lightest solution, keeps the longest, and is not coagulated on standing a week or two when mixed with various metallic mordants or tannic acid. A good gum will dissolve completely in its own weight of water, but many gums require at least double that quantity for their proper solution. Some samples are so soluble that, in the powdered form, they can be added directly to the printing colour, and will dissolve very rapidly therein if well stirred up for a short time. Most qualities, however, require boiling water for their complete solution, and in the case of Indian, Australian, and Cape gums, the boiling must be conducted under pressure, and even then complete solution is not always obtained without the addition of acetic or other acids.

In making a natural gum thickening, the gum is first stirred up with cold water for some time; the floating bits of chip, woody fibre, etc., are then skimmed off, and the whole is heated for several hours in a jacketed pan provided with agitators, which keep the gum from setting into a solid mass at the bottom of the pan. When the solution is complete, the hot thickening is ladled out of the pan into deep casks and allowed to stand several days for the purpose of allowing the sandy matter to deposit; the gum is then strained

and is ready for use. All gums contain sand and fine grit, and the longer their solutions can be kept in the casks before use the more likely are they to give satisfaction in printing; the finest grit is almost imperceptible, and takes a long time to deposit.

Besides testing a gum for its solubility, thickening power, clearness, and behaviour towards mordants, a practical printing trial must always be made. Many gums, although they fulfil all other requirements, cannot be made to give either a clean impression with sharply cut edges or a sufficiently bright colour, and in such cases the gum is absolutely useless for most classes of work. This is especially the case with gums which have been dissolved under pressure and contain a large proportion of insoluble matter. On cooling, the insoluble portion frequently settles out again in an extremely finely divided state; and although the thickening may appear to be perfectly homogeneous, it consists in reality of minute particles of gelatinous matter which are held in suspension by the thinner solution, and prevent the even absorption of the thickening by the cloth, thus giving rise to "fuzzy" prints.

Gum Senegal, gum arabic, gum gedda, and other thickenings of the same family, are best used by themselves. When mixed with starch, flour, or gum tragacanth they break up the thickening, deprive it of body, destroy its nature, and convert it into a slimy mixture, very apt to separate into its constituents during the printing process, and rarely or never giving satisfactory results, even if it happens to retain its original consistency. The addition of a small quantity of gum Senegal solution to starch and flour pastes is a common colour shop makeshift for softening and thinning colours that are too stiff; but it is a practice that is deprecated by most experienced colour mixers, and is only adopted to avoid the trouble of making up a fresh lot of thinner colour with a smaller quantity of the proper thickening.

Colours printed with gum Senegal and similar thickenings give beautifully even and transparent shades, but they come out much paler than when starch or gum tragacanth is used, and for this reason gum Senegal is mainly employed for the printing of light colours, and especially for those which form the ground or blotch of the pattern. The natural gum thickenings generally used for printing contain from 30 to 50 per cent. of solid gum, and consequently do not allow the colouring matter to penetrate very deeply into the fibres of the cloth. The result of this is that goods printed with gum thickenings lose a good deal of their colour in the washing and soaping operations that follow printing; and it is evident, therefore, that if very strong dark colours be printed with gum thickenings, the large amount of colour dissolved out during the washing of the pieces would seriously affect the brilliancy and purity of any other colours that might be associated with them, for the colours and mordants used in textile printing are extremely susceptible to the soiling action of any highly coloured wash-waters through which they may have to pass.

Gum Senegal and its class mix well with both strong alkaline solutions and with strong organic acids, a property which enables them to be used for all kinds of discharges, and resists, and for Indigo printing. But in practice they are usually replaced in these styles by the cheaper and more rapidly prepared British gum thickenings, which act quite as effectively in most instances.

Karaya Gum.—During the late war the shortage of cereals, and many of the gums, forced calico printers to make a more extensive use of thickening materials that had hitherto been more or less neglected. Among these Karaya gum (known also as Indian hog gum and hog tragacanth) has proved to be the most important. It belongs to the group of insoluble gums; that is to say, to the group of gums insoluble in water under the usual conditions. When

boiled with water under slight pressure it slowly dissolves ; when the pressure is increased the rate of solution increases and a useful mucilage is obtained. The disadvantages of working in this way are (1) that a special apparatus is required, and (2) that the gum is discoloured by the extraction of the colouring matter contained in the chips of bark always attached to the pieces of the cheaper and medium qualities of the gum. The better qualities are too expensive for calico printing. A more convenient method of dissolving Karaya gum, and one entirely free from the first of the above drawbacks, and almost free from the second, has been patented by the Calico Printers' Association, J. B. Fothergill and G. W. Wilson.[1] It consists in acting upon the ground gum with comparatively small portions of sodium peroxide, persulphate, percarbonate or persilicate. In presence of these bodies the gum is rendered perfectly soluble in boiling water, and at the same time is sufficiently decolorised for use as a thickening agent for printing colours. For finishing purposes it may be completely decolorised by a further treatment with bleaching powder.

The solution is effected in an ordinary jacketed colour pan, and quantities are as follows :—

100 kilos ground Karaya gum.
250 litres cold water.
0·3 kilo sodium peroxide.

Stir in the cold for 1–1½ hours ; then add

0·3 kilo sodium peroxide.
20 litres water.

Mix well, and in half an hour raise to the boil and continue boiling for 3 hours. Then cool, neutralise with hydrochloric acid (if necessary), and make up with water to 500 litres.

At this strength the Karaya gum is equal in thickness to a gum Senegal solution at 400 grms. per litre, and very much cheaper.

Karaya gum is suitable for all purposes to which gum Senegal and gum arabic are put in printing. It may also be used in finishing, but its importance in this connection has declined since, if used alone, it causes the pieces to curl when dry.

Dextrin and British Gum.—The terms *dextrin* and British gum are somewhat loosely applied to various descriptions of torrefied or roasted starch. What one maker calls " dextrin " another calls " dark British gum," and, in like manner, " yellow dextrin " is known also as " light British gum." The terms are also applied to the products derived from different kinds of starches, so that, taken altogether, they represent no definite compound, although, strictly speaking, dextrin is a definite degradation product of starch, obtained by heating it with dilute mineral acids, or by roasting it at a temperature of 160° C. until it becomes completely soluble in water.

From a practical printer's point of view, the difference between dextrin and British gum is largely a question of colour and thickening power. A dark-coloured product, easily and completely soluble in water, is generally described as dextrin, whereas a light-yellow or fawn-coloured product, containing a variable quantity of insoluble matter, is usually known as British gum. On the other hand, both are known as either dextrins or British gums, and, in point of fact, they may both be made from the same starch, the great differences in colour and solubility being entirely due to the duration of the roasting process. In the case of the dextrin or dark British gum this is continued until the whole of the starch is completely converted into a perfectly soluble and chemically true dextrin, while in the case of the yellow dextrin or light British

[1] English patent 120183, 1918.

gum the roasting is stopped before the whole of the starch is so converted. It is this unconverted, unaltered starch that forms the insoluble portion of all light British gums, so that when they are boiled up into pastes they really consist of a mixture of starch paste and dextrin solution. On the large scale, a small quantity of nitric acid is frequently mixed with the starch before it is roasted, and this affects its ultimate colour to some extent, but in the main this and the solubility depend upon the duration of the roasting. A highly torrefied starch gives a thin, dark brown solution; a lightly torrefied starch, a thick, light yellow paste, which requires boiling before it can be used as a thickening for printing-colours. The more starch a British gum contains, the more will its mucilage approximate to the qualities of starch paste and the less gummy will the thickening be; but all brands of British gums and dextrins can be mixed together in any proportion, and thus it is possible to vary the consistency and quality of the thickening in almost any way desired.

British gums are made from wheat, tapioca, and maize starches. For most purposes it is immaterial which starch is employed, but if a *yellow British gum* is to be used for thickening strongly alkaline colours like Indigo, a maize starch gum ought to be selected, as maize starch itself forms a much better thickening with strong alkalies than wheat starch. If dextrin or dark British gum is used in conjunction with strong alkalies, any brand may be taken so long as it contains no more than a trace of unconverted starch. Many recipes, made up with British gum and strong alkali, which work perfectly in one works cannot be worked at all in another. The explanation of this is that the British gum in the former case was made from maize starch, whilst in the other it was a wheat starch product.

With very few exceptions, British gums of good quality can be used for exactly the same purpose as gum Senegal, etc., the only drawbacks being that they give a somewhat yellower tone to pale shades, and leave the cloth a little harder in feel. On the whole, however, they are very valuable substitutes for the more expensive gums, and, if chosen and used with care, are capable of yielding perfectly satisfactory results.

British gum thickenings contain from 20 to 50 per cent. of dry gum according to the quantity of unconverted starch they contain; they are simply boiled in water and cooled without any further addition.

Locust Bean Gums.—During recent years mucilages prepared from the hard stone-like seeds found in the *locust bean*—the long sweet pod of the Carob tree—have been recommended as substitutes for gum tragacanth. The so-called "gums" from which these mucilages are made usually come into the market in powder form and, for the most part, consist simply of the finely ground decorticated seed. The greater portion of the residual husk is removed by screening, but the *germ* cannot be removed altogether in this way, and in ordinary locust bean gums it is almost invariably present. For mucilages that are to be used at once this is of no great consequence. On the other hand, if the mucilages have to be kept, as stock thickenings, it is a great disadvantage, since the germ promotes fermentation and the mucilage breaks up and becomes thin and watery.

Locust bean gums possess great thickening power; good qualities are 2½–3 times stronger than tragacanth in this respect and, consequently, where applicable, they are much cheaper than the latter. Such gums are sold under many different names, *e.g.* Gum Farinol, Gum Ghatto, Cheshire Gum, Diagum, etc.

Locust bean mucilages are best prepared by sprinkling the gum lightly into cold water, which must be stirred continuously to prevent the formation of lumps. The gum swells up quickly and forms a somewhat granular-looking

paste. When the whole of the gum is added, and thoroughly incorporated with the water (by stirring for some time in the cold), the mass is boiled until it thickens and becomes perfectly smooth and homogeneous. It is then strained to free it from bits of husk and other insoluble matters, and is then ready for use. A 1½ per cent. solution (about 2½ oz. per gallon) is suitable for most purposes, and is of approximately the same consistency as a 3¾ per cent. (6 oz. per gallon) tragacanth mucilage.

Any attempt to dissolve locust bean gums in the ordinary way by pouring water on to them, or by adding water little by little as is done in pasting-up starch or British gum, is doomed to failure; the gum simply forms a mass of unworkable lumps, each consisting of a core of dry gum enveloped in a thick sticky coating of partly dissolved gum, which effectually prevents the penetration of any water to the interior. Long-continued boiling and repeated strainings may result in the gum finally being got into solution, but the process is wrong. The addition of phenol or other disinfectant to locust bean mucilages retards decomposition, but is not a perfect preventive.

Tragasol.—Tragasol is a special product of the locust bean prepared by a patented process which effects the complete elimination of the active germ contained in the seed, and thus ensures a perfectly stable thickening agent. In this particular alone it is greatly superior to all other forms of locust bean gums; in fact, it is as stable as any thickening in general use. It comes into the market as a ready-made mucilage perfectly free from specks of husk and gritty matter. Several qualities are available, varying in colour from a transparent water-white to a pale straw. The two qualities most suitable for printing purposes are the P.C.D. and C.S. brands; they are both clear and colourless, and the former—the P.C.D.—is specially filtered.

Tragon is a concentrated tragasol in the form of a dry powder. For some purposes it is more convenient than tragasol, but apart from that it possesses no other advantages. Tragon is dissolved in exactly the same way as the ordinary locust bean gums, *i.e.* by sprinkling into water, etc., as already described. It gives a thick, clean mucilage free from insoluble matter and, as might be expected from its mode of preparation, of good keeping properties.

The use of tragasol and other locust bean products as substitutes for tragacanth is of limited application. Alkalies and tannic acid convert all such gums into ropy masses, and the behaviour of these gums in mixture with metallic mordants leaves much to be desired. In the case of these latter, and also of tannic acid, a considerable addition of acetic or other organic acid improves the working-qualities of the printing colour, but the cost of this excess of acid more than neutralises the cheapness of the gum.

So far as printing is concerned, the chief use of locust bean thickenings is in the printing of diazo-solutions, "acid resists," and Acid colours on wool and silk. A special use of tragasol is connected with the application of vat colours by spraying and screen, block and roller printing, and will be described in the section dealing with vat colours.

Tragasol and other similar mucilages find extensive use in the finishing of both white and printed fabrics and are, perhaps, of more value in this connection than as thickeners for printing colours.

Colloresine D.K.—Unlike the natural vegetable thickening agents, already described, Colloresine is a synthetic product. It is a methyl ester of cellulose, prepared from cotton, and in its original form (Colloresine D.) it was placed on the market in a loose fibrous state, resembling raw cotton in appearance.

Colloresine D.K. represents an improved and concentrated form of Colloresine D. dry, and possesses about double the thickening power of the latter. It is also a fibrous substance, but unlike the original brand it is compressed into

cakes of approximately 1, 4, and 10 lbs., which swell quickly in warm water, and go into complete solution when stirred and allowed to stand a few hours.

The most remarkable and valuable property of Colloresine D.K. is that it is insoluble in boiling water, and also in the presence of fixed alkalies. On heating a solution of Colloresine the substance is precipitated, but on cooling it again goes into perfect solution. Thus printing colours thickened with Colloresine D.K. neither "mark-off" nor "bleed" during the various after-treatments, in steam and hot solutions, to which the printed goods are subjected for the development and fixation of the colours. The heat of the processes coagulates temporarily the thickening which, in this state, holds the colouring matter firmly in place on the cloth until its chemical fixation is complete. The thickening is then easily removed from the cloth by simply washing in *cold* water, in which the coagulated Colloresine readily re-dissolves.

Additions of alkali carbonates and caustic soda in concentrated solutions, phenols, tannic acid, and neutral or basic metallic salts all cause Colloresine thickenings to settle out in flakes. On the contrary ammonia and dilute caustic soda have no effect on the thickening; and additions of the sulphocyanides of potash or ammonia, of organic acids such as acetic, lactic, or tartaric acid, of glycerine, alcohol, Glyecine A. and other organic solvents, and of such organic compounds as Solution Salt, Ludigol, and Dissolving Salt B., actually promote the swelling of Colloresine and improve the body and viscosity of its solution.

Consideration of these properties indicates the class of work for which Colloresine is best adapted and demonstrates its advantages over the usual thickening agents in some directions and its disadvantages in others.

For example, it is unsuitable for the printing of Basic Dyestuffs, and all printing mixtures of a strongly alkaline nature, such as those employed in the *usual* processes for the printing of vat colours. On the other hand, its characteristic behaviour under the influence of heat has led to the introduction of an entirely *new* and valuable process for the printing of vat colours—a process of particular interest to block, screen, and spray printers, because, unlike the usual processes which require the printed goods to be developed as soon as possible after printing, it allows of the prints being kept, without detriment, for any length of time *before* development. This advantage applies equally both to roller printing and to surface printing from cylindrical blocks, and is a great convenience in every way. Another important advantage of the Colloresine process is that printing colours free from alkali may be used, thus preserving unimpaired the quality of the printing blankets, back greys, copper rollers, silk stencils, felted blocks, brushes, and other accessories employed in the various methods of printing.

The properties of Colloresine are also of advantage in the printing of Chrome mordant colours and of the insoluble azo-colours produced on the fibre, on account of the fact that it is so easily washed out, leaving the cloth softer and of better feel than is the case with gum or starch thickenings.

Colloresine thickenings retain an invariable and satisfactory consistency; they are perfectly stable, never becoming mouldy, sour, or watery; and they may be mixed in any proportion with any of the vegetable thickenings in ordinary use.

Sericose.—About eighteen years ago the Farbenfabriken vorm. F. Bayer & Co. patented a method of preparing the acetyl derivatives of cellulose, one of which, Sericose L., was used as a combined thickening and mechanical fixing agent for the printing of such substances as bronze powders, mica, and pigments. For this purpose, when suitably dissolved, it is a simple and reliable medium. Sericose is insoluble in water, but may be dissolved in acetic acid

of 8° Tw., though dilution with water precipitates it. It yields better solutions with acetone, mixtures of acetone and phenol, and with other organic solvents, many of which have been employed at different times in practice. The best preparation of acetyl cellulose for use in printing is a solution of Sericose L.C. Extra (an improved brand of Sericose L.) in Sericosol A., a special solvent, free from the disagreeable and irritating odours of the more volatile solvents. Sericosol A. is a neutral, clear, colourless and odourless liquid, boiling at 345° F.; it is a perfect solvent for Sericose L.C. Extra, and evolves no fumes injurious to the health of the operatives.

The presence of water in the solution must be avoided as much as possible. Even when used with pigments in paste form the water content of the paste must be adjusted so that it does not exceed 25 per cent. of the whole. The thickness of the Sericose solution or paste may be reduced by the addition of more Sericosol or by alcohol, cyclohexanol, or a special solvent sold as Solvent E. 13.

The application of Sericose L.C. Extra will be described in a later section dealing with the printing of pigments.

Albumen.—Albumen is obtained from the whites of eggs and from the serum of blood. Both these substances are evaporated to dryness at a gentle heat and under reduced pressure, and they come into the market in the form of thin, small scales: egg albumen, quite transparent and of a pale yellow colour, and blood albumen, semi-opaque and from light to dark brown in colour. Albumen is soluble in water, and can be coagulated either by heat alone or by warm mineral acids—two properties which enable it to be used as a mechanical fixing agent for pigment colours and certain insoluble lakes. Egg albumen coagulates at a temperature of 75° C.; blood albumen between 73° and 80° C. Blood albumen is cheaper than that obtained from eggs, but its dark colour prevents it from being used for delicate tints, for which egg albumen must always be employed. Various processes have been tried for bleaching blood albumen, but so far without any conspicuous success; it can be improved in colour to some extent by the action of turpentine, and it is always advisable, for other reasons, to add a little of this to the solution.

Albumen is best dissolved in tepid water, 20°–25° C., the usual strength of the solution being anything from 35 to 50 per cent. At the latter strength it gives (after straining) a good gum-like thickening, which mixes in all proportions with gum tragacanth. Pigment printing colours and colours for Indigo discharge styles usually contain 12–15 per cent. of albumen, which is quite sufficient to fix them. Formaldehyde forms an insoluble compound with albumen, but this reaction is more interesting than useful, and is rarely applied practically in textile printing.

In dissolving albumen, 200 lbs. are mixed with 30 gallons of water and well stirred up for a few minutes; the whole is then allowed to stand twenty-four to thirty-six hours (being again stirred up every few hours), when, if the albumen is of good quality, the solution ought to be complete.

The addition of ammonia or borax facilitates solution, and in warm weather it is usual to add a little phenol or other disinfectant to retard the decomposition to which albumen solutions are liable.

Apart from its use as a mechanical fixing agent for pigments and lakes, albumen finds but little application in a modern printworks. It is employed occasionally for waterproofing the wash-blankets of printing machines, but this use is by no means general, and probably the albumen could be replaced with advantage by other substances.

Casein and Lactarine.—Casein is the essential constituent of cheese, and closely resembles albumen in many properties. It is obtained by acting on

skimmed milk with rennet or an acid, either of which throws down a curdy mass—casein—which, after repeated washings in tepid water, is dried at a gentle heat, and put on the market in the form of a yellowish-white powder. It is insoluble in alcohol, and in hot or cold water, but dissolves easily in warm, slightly alkaline solutions, and if a sufficient quantity is taken it gives a thick, smooth paste, very suitable for machine printing. Casein is used in exactly the same way as albumen for the fixation of pigment colours, but it is not so good for the purpose, as the colours do not resist washing to anything like the same extent as do those fixed with albumen, and if the soap used contains free alkali they can be removed almost entirely from the cloth. Formaldehyde acts very energetically on casein, forming an insoluble compound which fixes pigment colours much more permanently than when the casein is simply steamed. In order to make use of this reaction the pigments are ground up with a casein paste and printed in the usual way; the goods are then either padded in a solution of formaldehyde, dried, and steamed a short time, or are passed through a chamber containing hot steam and formaldehyde vapour. In either case the casein is coagulated, and encloses the pigments in a sort of insoluble envelope, similar to that produced by the steaming of albumen. The colours so fixed resist washing almost, if not quite, as well as albumen colours, and are equally bright and "toppy"—that is, they stand out well.

Notwithstanding this, casein has never replaced albumen to any considerable extent, probably because the latter is much simpler in its application, and, taken altogether, produces better and more reliable results.

The alkali generally employed in dissolving casein is borax, which answers the purpose perfectly, and has no effect on the shade of the pigments with which it is mixed.

Lactarine is to all intents and purposes identical with casein, and is applied in the same way. Some samples contain borax, and therefore only require warm water for their solution.

Glue.—Glue (an animal substance obtained by boiling bones, etc., in water) comes into the market in the form of hard, transparent, dark brown cakes. It swells up in cold water into a soft gelatinous mass, which dissolves completely on gently heating. Formerly it was employed for the printing of metallic powders, being mixed with starch and printed as a hot paste, upon which the powder was dusted before the glue set; but at the present time its use as an addition to thickenings is limited to a few resist pastes. It is chiefly used now as an addition to the dye bath, for the purpose of preserving the purity of the "whites" in the madder and other dyed styles.

China Clay, pipe clay.—China clay or kaolin is not a thickening agent as such; but as it enters largely into the composition of resist and discharge colours, it can be most conveniently mentioned here. Its function in printing pastes is to prevent the acids, etc., from spreading or running, and it also acts as a mechanical resist, and thus aids in the production of the effect desired. It ought to be white when ground up with water, and free from all gritty particles.

China clay is added to gum or starch thickenings in paste form (50 per cent. paste), and is boiled up with them in order to incorporate it thoroughly with the other ingredients. Acid resists and various discharges contain from 10 to 20 per cent. of china clay, according to the quantity of water used and the kind of acid employed. Citric acid and citrates are extremely liable to spread during the steaming process, and they require more china clay than most other substances used for similar purposes.

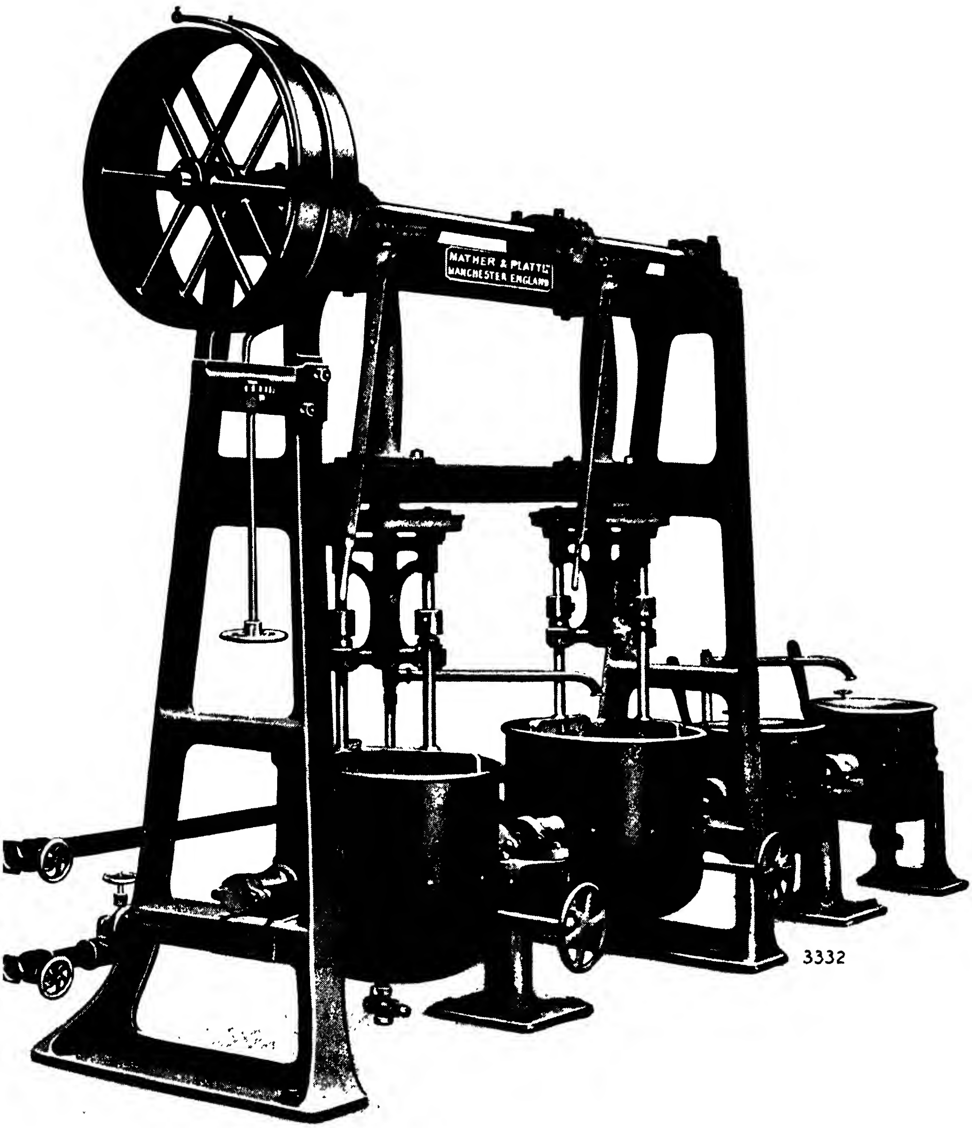
China clay is also largely employed for "back filling" printed goods, and in other operations connected with the finishing of woven goods.

THE MAKING OF PRINTING COLOURS.

Generalities.—The colour shop, as the colour making department is usually designated, should be a large, well-lighted room, situated on the ground floor of the works, and, for convenience, as close as possible to both the "drug" room and the machine room. It ought to have a flagged or a concrete floor, and should be well ventilated above to allow the steam and acid vapours disengaged during the boiling of colours to escape freely into the outer air; it should also be well drained to carry off all waste waters and liquors, and, above all, should be provided with a copious supply of pure, clean water. In many establishments the whole of the condensed water produced in the many drying machines of the various departments is collected and utilised in the colour shop for the preparation of mordants and colours. There is nothing better for this purpose than condensed water; it is clean, soft, and pure, and, in addition to giving the best colours, it represents a considerable saving in steam. The high-pressure steam used for driving the machinery is run through reducing valves into a low-pressure range of pipes instead of escaping into the air, and thence into the drying machines, from which a large proportion of it issues, as condensed water, at a comparatively high temperature. The utensils used in colour making or colour mixing are neither numerous nor complicated. They consist of boiling pans of various capacities, of storage casks, tubs for transporting the colour to the machine room, scales, measures, stirring sticks, and different qualities of straining cloths, together with cisterns and becks for washing such of the articles as are portable. In most colour shops, too, there are grinding mills for pigment colours, Indigo, and other insoluble substances and, where large quantities of Aniline black and Madder colours are used, mechanical straining machines through which 15 to 20 gallons of colour can be passed at once.

The boiling and cooling of the colours is effected in double-cased pans of copper, steam or cold water being made to circulate between the two casings, according as the colour is to be boiled or cooled. The larger pans are provided with two mechanical agitators which keep the colour in constant motion, and thus ensure a smooth paste and the perfect mixing of its ingredients. The agitators turn on their own axes and at the same time travel continually round and round the interior of the pan, so that every particle of colour, except that which cakes on the sides of the pan, is thoroughly stirred up. They are worked on the well-known sun and planet system, and are actuated by bevel gearing and a vertical shaft (see Plate VII.). The latest colour pans are made to swing, for convenience of emptying and cleaning, and they can be tilted to any desired angle by means of a toothed wheel which gears into a screw worked by hand. The toothed wheel is fixed on one of the two hollow trunnions upon which the pan swivels. One end of each of these trunnions communicates with the space between the double casing of the pan, and the other fits into a stuffing box carried by a short hollow pillar. Each pan is thus supported on two hollow pillars (one at each side), one of which is connected to the steam supply and the other to the water supply, and, through their respective trunnions, both communicate with the space between the casings, so that either steam or water can be introduced as required (see Plate VII.).

Printing colours are made up in two different ways. The first method is to boil the thickening agent and colouring matter or mordant together; the second, to mix either hot or cold solutions of the colouring matters or mordants with a previously prepared thickening. In many cases it is quite immaterial which method is employed, but some colours always require boiling, others are better boiled, and yet others again can only be prepared with ready-made



Double-cased Copper Pans.

[*To face p.* 142.

thickenings, and often only in the cold. Wherever possible, and when only small quantities of colour are required, it is preferable to make use of the second method ; it is more convenient, and the colours can be prepared more quickly. On the other hand, when *large* quantities of a colour that *can* be boiled are required it is always better to boil it, because large quantities can be much more thoroughly mixed in a pan with mechanical agitators than by raking or stirring up in a cask by hand (especially if the colour be at all thick), and further, because the whole batch of colour being of exactly the same thickness and shade throughout, will give perfectly uniform results in printing, whereas if it were mixed in small separate lots it would be likely to vary somewhat in both consistency and depth of shade.

Direct-dyeing colours and basic aniline colours can be prepared by either method ; but when they are very strong or deep they are better boiled, for the simple reason that the quantity of water (and acid) required for their solution, and for that of their mordants, would be so great as to thin down the thickening paste to a point unsuitable for printing.

Dyewood extracts can also be mixed by either method, but they generally work better when boiled up with the thickening ; and Logwood is always much better boiled than when mixed in the cold with starch or any other paste. Alizarin, too, gives brighter shades when boiled with its thickenings, but it and also the extracts of Quercitron bark and Persian berries are, as often as not, mixed with cold ready-prepared thickenings, and the results obtained in this way quite justify its adoption. Many so-called Alizarin colours are in paste form, finely ground, and can be readily dissolved in cold starch paste or gum ; and Alizarin blue S. is so extremely soluble that it can be added, as a dry powder, directly to its thickening, in which it dissolves at once. Auramine and several other colours decompose on boiling, and must therefore be added to their thickenings at a lower temperature ; pigments and diazotised bodies can only be compounded in the cold, the first because their thickening (albumen) is coagulated by heat, and the second because diazo-compounds are excessively unstable at the ordinary temperature, and must be cooled by ice or other means.

These are a few examples of the general methods employed for combining colouring matters and thickening agents ; but as each of the above colours merely represents a class, each member of which possesses its own peculiar properties, it will be easily seen that before any particular colour can be properly thickened its special characteristics must be thoroughly studied, so that it can be prepared in the best, most convenient, and cheapest way. There is a good deal of latitude in colour mixing ; each colour mixer adopts the method that yields him the best result, and no two work on quite the same lines ; each adapts, and must adapt, his methods to the conveniences at his disposal, and to the demands made upon his department. A colour mixer ill provided with pans cannot hope to keep pace with the printing machines if his system of working depends upon the keeping in stock of a large number of boiled colours. He must make up as many of his colours as possible in the cold, and to this end he utilises his pans for the preparation of large quantities of those thickening pastes that are most generally useful, confining his boiled colours to the few that cannot well be prepared in any other way. On the other hand, in a well-fitted colour shop many colours are boiled that could be satisfactorily made up in the cold, and for this reason—that in boiled colours no uncertainty exists as to the complete solution, and even distribution of the various constituents, whereas in mixed colours made up from cold pastes it frequently happens that the colour is both imperfectly mixed and "specky," that is, it contains particles of undissolved colouring matter which show up in the finished print as minute points of dark colour. On the whole, however, the tendency nowadays is to

boil as few colours as possible, and, except in small works devoted to the production of one or two special styles, a constantly increasing number of colours is made up from previously prepared thickenings. This tendency is the direct outcome of the introduction of artificial, synthetically prepared, dyestuffs. In former times the number of colouring matters at the disposal of the calico printer was comparatively small, and large quantities of a few colours only were consumed, the bulk of the work being produced in what is known as the dyed way. At the present time the reverse is the case, small quantities of an enormous number of colours, diverse both in shade and properties, being in daily demand. The result is that the sum-total of the colour consumed in a modern printworks is distributed over so vastly increased a range of colours that it is virtually impossible to work on the old lines of boiling large quantities of stock colours. The boiling of a colour occupies (with the cooling) the better part of two hours at least, from which it is evident that, if the majority of modern printing colours had to be boiled, an enormous number of pans would be required, not to speak of the extra floor space that would be needed for storage purposes, or of the time lost by the machine printer in waiting for his colours. Moreover, all printing colours are better, in most respects, when freshly prepared. When kept for any considerable length of time they all deteriorate in one way or another: either they lose their tinctorial strength, or their thickenings decompose or otherwise become unworkable. Starch and flour pastes become sour and thin; albumen decomposes; British gums set into a solid mass; natural gums are apt to be coagulated by the substances mixed with them; and the constituents of colours which contain all the elements that are necessary to the formation of an insoluble colour lake are liable to combine more or less, and thus form in the colour paste itself the lake that ought to be formed on the fibre. For these reasons it is inadvisable to prepare an unnecessarily large stock of any colour, which, although in constant demand, is only worked off in comparatively small quantities at a time. The only colours that are made in large quantities and always kept in stock are those which keep exceptionally well, and which enter largely into the majority of the various colour combinations of most of the patterns printed. These colours are known as standards; and in works where a large amount of cretonne and other heavy styles of printing are carried on—styles which are executed, for the most part, in the same range of colours—a good supply of such standards is necessarily kept on hand, since they are not only used alone, but also in combination with other colours to form compound shades, such as olives, browns, greys, etc.

Fortunately, the greater number of artificial dyestuffs now sent out by the best aniline colour firms are eminently adapted for mixing with previously prepared pastes.

They are very soluble and of great tinctorial strength, a combination of properties which makes it easily possible to prepare full, deep-printing colours in this way without making the thickening paste too sloppy to work properly in the machine. The amount of colour solution required to produce a dark colour is so small, as compared with the quantity of paste used for thickening it, that the printing quality of the mixture remains unimpaired, and in most cases the results are indistinguishable from those yielded by a boiled colour of the same strength and consistency.

All thickened pastes that are printed on woven fabrics are technically known as "colours," whether they contain any colouring matter or not. Some colours contain only a thickening agent and a mordant; others, a thickening agent and a colour; others, again, contain all three; and yet others are nothing but thickened mixtures and solutions of various substances that are used for the

purpose of producing discharges or of preventing the permanent fixation of any colour upon those parts of the cloth upon which they are printed.

The preparation of printing colours by the two methods already mentioned can be most conveniently explained by describing the making up of a steam colour—that is, a colour developed and fixed on the cloth by a passage through hot steam. Steam colours consist essentially of four parts:—

(1) The solvent.

(2) The colouring matter.

(3) The thickening material.

(4) The mordant or fixing agent, which forms an insoluble lake with the colouring matter.

These four component parts may be either simple or compound—that is, they may, and frequently do, consist of one, two, three, or more members of their class, according to circumstances, and to the effect that their combination is required to produce. The more complex colours will be dealt with in detail in another section of this volume; for the present purpose it is sufficient to take a simple example which will illustrate the general methods of making up a printing colour.

Suppose, for instance, that it is required to prepare a printing colour containing 2 per cent. of Methylene blue which is to be thickened with starch and fixed with tannic acid. In this case the solvent used is generally a mixture of water and acetic acid, together with a small percentage of tartaric acid. If the colour is to be boiled, the *modus operandi* is as follows:—2 lbs. of Methylene blue and 1 lb. of tartaric acid are placed in a small pan and dissolved in 1 gallon of water and 1 gallon of acetic acid; whilst this is going on, 12½ lbs. of starch are stirred up in a ten-gallon pan with 7 gallons of water; the colour solution is then added to the creamy starch and water in the larger pan, and after further adding ¼ gallon of rape or olive oil the whole is boiled until the thickened paste just begins to thin down again; at this point the steam is turned off and water turned into the space between the casings of the pan for the purpose of cooling the hot paste; when the paste is cold, 5 lbs. of tannic acid, previously dissolved in ¾ gallon of either water or acetic acid, is added to it, and after it is thoroughly incorporated the colour is ready. The above quantities make 10 gallons of colour, which correspond in strength to a 2 per cent. solution of Methylene blue.

The preparation of the same colour from ready-made paste calls for little description. Seven gallons of thick starch paste are first measured into a tub; 2 gallons of a 10 per cent. solution of Methylene blue, in acetic and tartaric acids, are then poured into it through a fine silk or sateen sieve, a little at a time, each portion being well mixed with the paste before the next is added; when all the colour solution is added, 1 gallon of a 50 per cent. solution of tannic acid is stirred in, and the whole is then ready for use as a printing colour.

Pigment colours and other insoluble substances are usually ground up in a mill with their respective thickenings, any additions being made afterwards; or they are added to their pastes in the form of finely ground mixtures (with water, etc.) of a creamy or buttery consistency. Both methods are used, but the former is the more reliable, and is always employed in works furnished with the necessary grinding mills.

With very few exceptions, all printing colours are prepared by one or other of the above general methods; modifications are, of course, introduced in many cases in order to comply with the conditions under which certain colours and mordants must be compounded, but these are questions of detail rather than of principle, and wherever they arise in the following pages they will be noted in connection with the particular styles with which they are associated.

Some colouring matters are capable of forming several different lakes with

different metallic salts, and others combine very rapidly with their mordants. In both these instances the colour paste is made up without the mordants, which are added afterwards as required. It is not absolutely necessary to proceed in this way, but it is both the most convenient and most economical system to work upon, because it enables the colour mixer to obtain several effects from one standard paste. For example, Persian berry extract forms with certain tin mordants a strong and brilliant orange lake; with other tin salts it gives a bright yellow; with aluminium and tin it gives another tone of bright yellow; and with chromium mordants it yields a strong yellowish-brown; all of which shades can be produced from one standard of thickened Persian berry extract by simply adding the different mordants as required.

Alizarin blue is another colour that yields different shades according to the mordant used. Copper acetate gives reddish-blue, very fast to light; chromium acetate, a quiet, somewhat less reddish shade, also fairly fast to light; nickel acetate, a much purer blue, fast to soaping, but not very fast to light; zinc sulphate, a still purer and brighter blue, similar in other respects to the last; and manganese salts, a bright, quiet shade of blue, much greener than any of the preceding. All these different mordants act very rapidly on Alizarin blue, so much so in fact that fully made-up colours will not keep good for more than two days at the outside. Alizarin itself is perhaps the most typical of this, *the adjective,* class of colouring matters, since it gives entirely different colours with aluminium, iron, chromium, and tin mordants; but, with the exception of the reds and pinks that are made from it, it is made up in one of the two ordinary ways. The reds and pinks are unstable, and are usually prepared fresh each day.

Formerly it was the custom to manufacture most of the various dyewood extracts, mordants, and other liquors used for colour making in the printworks itself. At the present time, however, the making of colouring matters and extracts is a separate industry, which has been developed to such an extent and brought to such a pitch of perfection that its products can be bought in the market at a much cheaper rate than they could possibly be made in any printworks. One or two vegetable extracts and a few simply made colouring matters are still manufactured occasionally in some printworks where the necessary plant exists, but, generally speaking, the whole of the raw material of calico printing which requires special plant, and a specially trained staff of chemists for its manufacture, is now bought ready-made, and in a condition fit for immediate use. Synthetic dyestuffs, in particular, could not possibly be made at a profit, and in any quantity, in a printworks. For their manufacture on a commercial scale they demand not only a specialised knowledge of the subject, but the constant supervision of experienced expert chemists, who are thoroughly conversant with every detail of the various stages through which the raw material passes. Synthetic dyestuffs, then, must be bought as such, but this does not apply, except in a few cases, to the mordants and other preparations which are used for fixing them on the cloth, or for enhancing their brilliancy and effect.

These are always made on the spot in all printworks of any standing: their composition is then known, and they can be modified at will and without any trouble. Besides, they are cheaper, because they entail no charge for the carriage of mere water, which constitutes the greater part of their weight. Mordants possessing all sorts of extraordinary advantages can be and are bought by the score, but they are best left severely alone. Their composition is usually disguised under a fancy name; and even if it be given, it will be found frequently to represent only partially what the "stuff" contains. Many of these mordants are quite good and answer their purpose perfectly, but none of

them, unless they be patented articles, are any better than those made by a capable printworks chemist, and, in addition to being more expensive than the latter, they cannot be modified until their composition has been ascertained by a more or less lengthy analysis; in a word, such mordants, etc., are unnecessary additions to the cost of production, and ought to be avoided, on all counts, if at all possible. Such products as tannic acid cannot be made in the colour shop, but most of the other mordants and preparations in common use can and ought to be made there, partly because they are cheaper to make than to buy, partly because they are more regular in composition, and partly because the colour mixer then knows exactly with what he is working, and can thus alter his colours at once, and in the best way, for any special purpose.

Working instructions for the making up of the more important mordants, etc., will be given in the section on Mordants.

Straining of Colours.—No matter how carefully colours have been made, they always contain either lumps and hard pieces of thickening, or foreign insoluble substances, which give rise to imperfect printing if allowed to remain. A certain amount of thickening invariably cakes on the sides of the colour pan during the boiling process, and portions of it are unavoidably detached and fall into the colour when it is emptied out, making it lumpy; and, again, when colours are kept in stock, a skin of dried thickening forms on their surface, and although this can be skimmed off to a great extent, portions of it are liable, nevertheless, to become incorporated with the smoother paste beneath. Another cause of lumpy colour is due to the drying of the thickening on the sides of partially empty storage casks: the dried paste forms hard, brittle scales, which drop off into the colour below. The foreign insoluble bodies usually present in freshly prepared printing colours consist, for the most part, of grit, chips of wood, woody fibre, leaves, sand, and particles of metal—small quantities of all of which are apt to get into thickening materials and colouring matters during the process of manufacture. Natural gums are especially liable to contain sand and woody fibre, as might be expected from the way in which they are collected; and substances that come into the market in the form of finely ground powders are also exceedingly liable to contain all sorts of grit and dust, which no amount of care can entirely prevent from settling upon them whilst they are kept in stock. Particles of metal are also mixed with them during the operation of grinding. In the case of gums and substances that are used in solution, the greater part of the gritty impurities can be eliminated by allowing them time to deposit; but with thick pastes like starch and some of the dyewood extracts this cannot be done, and the only way to get rid of solid impurities is to strain them out. Some low qualities of starch and British gum contain a peculiar organic body which is disseminated in an insoluble form throughout the entire thickening and cannot be removed in any way. The finer parts of it pass through the straining cloth, and, in printing, they fill up the engraving with a sticky glue-like paste; the coarser parts stick in the meshes of the straining cloth and gradually fill them up with a gelatinous mass, which effectively prevents the passage of the colour, and renders straining impossible. Such thickenings are absolutely useless, and ought to be returned to the vendor at once.

Colours are usually strained by hand directly into the tub that is to be sent into the machine room. A piece of calico is spread over the tub and the colour poured into it; the ends and edges of the calico are then gathered up in the left hand of the operator so as to enclose the colour in a sort of bag; this bag is now twisted with the left and squeezed with the right hand until its contents have passed through, leaving behind only such portions as are too large to escape through the meshes of the calico. If the colour is very rough to start

with, or contains a good deal of grit, it is strained through one cloth into another, as many cloths being used as are thought necessary, and each one being finer in texture than the one preceding it. The advantage of using a series of graduated strainers is obvious: any large, soft lumps of thickening are broken up in passing through the coarser cloths, the bulkier pieces of hard starch, undissolved gum, or dried scales of colour are removed at the outset, and the paste gradually becomes smoother and smoother, until it will finally pass through the last and finest cloth almost unchanged.

Very lumpy colour, or colour composed of several standard colours roughly beaten together in the mixing tub, cannot be properly strained through one cloth, however fine. The lumps squirt through the interstices in little worm-like masses, which cannot be beaten into a smooth paste, and mixtures of different colours, especially if they be of different thicknesses, are always better when strained twice at least, since the act of straining goes a long way towards mixing them into a homogeneous paste.

Various kinds of mechanical strainers have been put on the market from time to time, with the object of replacing, or at least reducing the amount of, hand straining. So far, they have failed to do this to any very great extent, not because they are not efficient so far as straining *per se* is concerned, but because they can only be used with advantage when large quantities of one colour are required by several printing machines at the same time. In an ordinary modern printworks, doing a great variety of styles, these occasions are of rare occurrence (once or twice a year maybe), so that, unless the straining machines are used for the needless straining of standard pastes and colours, which always have to be strained again before use, they stand idle for the greater part of the time. On the other hand, they are exceedingly useful to those firms who turn out large quantities of Indigo, which is not easily strained by hand, and of madder work—a style in which but few printing colours are used, and those regularly and in enormous quantities. Madder colours are always boiled; and they are frequently consumed at so great a rate that there is no time to cool them before printing, if the printing machines are to be kept constantly running. In such cases a straining machine, capable of straining fifteen or twenty gallons of almost boiling colour in a couple of minutes, is of inestimable value, and can scarcely be dispensed with. There is no constructional reason why straining machines should not be used for small lots of colour; but, considered from a practical point of view, they are altogether useless for this purpose, for the simple reason that they require thorough cleansing every time a fresh colour is put through them. More time would thus be occupied in washing them out than in straining colour. Apart from loss of time, machine-strained colours are only suited to comparatively coarse work, so that in any case straining by hand must be resorted to for delicate engraving, and for all designs of the highest class. The better a colour is strained the better will it work, and the more perfect will be the final result.

Defects in Printing Colours.—Apart from accidents, defects in colours may be attributed to (1) bad straining, (2) faulty or careless mixing, (3) to the colour being too thin or too thick, (4) frothing, and (5) "sticking-in."

(1) BAD OR INSUFFICIENT STRAINING is answerable for that kind of bad work which consists of streaks and snappers, both of which have been mentioned already in dealing with roller printing. However carefully a thickening is made it is liable to contain solid substances, which, if allowed to remain in the colour, become jammed between the doctor and the roller and, by lifting the former out of contact with the latter at the particular point where the obstruction happens to be, allow a certain amount of colour to escape the cleaning action of the doctor, and thus cause a long, unsightly smear, varying in width

according to the size of the obstruction in question. Such defects are known as snappers or snaps from the sharp sound made by the doctor in returning to its original position on the roller when the hard particle escapes from under it. In addition to lifting the doctor blade, these solid particles of grit either snip the doctor edge or scratch the plain surface of the roller, thus producing streaks —fine lines—which ought not to appear at all. Loose filaments of cotton and lint, left in the colour from a previous printing, also give rise to streaks and snappers in the same way—that is, by sticking between doctor and roller. Fortunately they neither injure the roller nor spoil the doctor edge, but they usually give much broader smears ; and if they happen to stick on an engraved part of the roller, they prevent it from taking up colour, and consequently that portion of the pattern fails to appear on the cloth. The only remedy for these defects is to re-strain the colour, and make perfectly certain that it is quite free of all foreign matters before it is returned to the printer. Any particles of finely divided copper that may be left in the straining cloth have found their way into the colour in the machine room, and their presence is to be put down to the roller grinding against some hard substance with which it ought *not* to be in contact.

(2) Faulty Colour Mixing.—It frequently happens that printed colours, instead of being perfectly flat and even in tone, present a mottled appearance, due to the presence of numerous and minute specks of dark colour. These specks may be caused in newly made colour by imperfect solution of the colouring matter ; by the insufficient sieving of pastes, like Alizarin, etc., before they are added to the thickening ; by not grinding insoluble lakes and pigment colours finely enough ; and by irrationally mixing together colours or mordants which mutually precipitate each other. A particularly flagrant instance of the last cause of specky colour occurred in a large and old-established printworks near Manchester, where the foreman colour mixer attempted to modify the shade of a steam Alizarin colour with lampblack ground up in albumen. The formation of specks in colour that has been used previously with satisfaction is due to the precipitation of the colouring matter by the mordant: it occurs chiefly in old, basic aniline colour pastes, Alizarin colours, and in various mixtures of these with each other and with natural dyestuffs. There is no way of remedying specky colour ; and the only way of preventing it is to see that the colour is prepared properly in the first instance, and to avoid using colours that have been in stock a long time—at least, such as are liable to decomposition.

Very often colours made up with mixed thickenings cause a great deal of trouble in working. They may appear to be all right at first, but little by little the thickening separates into its constituents, which, being of different consistencies, are absorbed unequally by the cloth, thus causing bad work in the way of cloudy, uneven colour. Sometimes this separation of the thickening is caused by the chemical action of the various substances contained in the colour, and cannot always be foreseen ; but generally it is the result of carelessness (or ignorance) on the part of the colour mixer, in mixing together such things as starch and gum Senegal, or flour and gum arabic, both of which combinations are excessively unstable when mixed in the cold, and are always unreliable even when boiled together. Flour, starch, and gum tragacanth work well together ; also starch and the British gums ; but the latter ought not to be mixed with tragacanth unless they are very starchy, and even then they are apt to separate out again. The natural gums—Senegal, gedda, arabic, and the more insoluble sorts—are better used alone, as they very rarely work well with any thickening outside their own class.

It is scarcely necessary to point out that compound shades made by mixing

two or more standard colours together, and colours reduced in strength by the addition of extra thickening paste, must be always well stirred up in order to ensure their perfect incorporation. Any neglect of this elementary precaution results in uneven printing, and is inexcusable in an experienced colour shop hand. With strong pigment colours it is often quite impossible to maintain the homogeneity of the colour, especially if it has to be used thin. Heavy bodies like vermilion and the lead chromates cannot be prevented from settling to the bottom of the tub, or, if in the printing machine, to the bottom of the colour box. All that can be done to lessen this great disadvantage is to use only the most finely ground pigments, to make the printing colour as thick as is consistent with the work in hand, and to stir it up well at frequent intervals, both in the tub and in the colour box of the machine.

(3) Thin and Thick Colour.—The consistency of a colour exerts considerable influence on the quality of the impression produced by the engraved roller or block upon the cloth. Within certain limits the printer is the best judge of the thickness of colour required for certain styles of work and different scales of engraving, and wherever possible he ought to be supplied with the sort of colour he thinks he can work with best. But it is no part of the printer's duty to dictate the kind of thickening material to be used in any given case, although, if he be an experienced workman, any suggestions he may make respecting the working quality of the colour will, as a rule, be considered, if they are at all reasonable. At the same time no printer is expected to interfere with the working of any department outside his own, neither is he justified in ordering a particular colour on his own authority, nor in refusing to give a trial to a gum colour simply because it is *apparently thinner* than a starch colour that he has just successfully printed with the same roller. It is impossible for anyone by mere inspection to estimate with any degree of certainty the relative printing qualities of two colours that are thickened with totally different materials. Gum thickenings rarely or never appear to be as thick as starch, flour, or tragacanth pastes; but thickness, considered merely as stiffness, is not the only desirable quality in a printing colour. It must also possess a certain body, and this, to a great extent, is dependent upon the density and viscosity of its thickening; in other words, upon the percentage of dry thickening material it contains, and upon the nature of that material. Gum solutions often contain three or four times more dry thickening than starch and other similar pastes, and consequently gum colours frequently give a much crisper and more perfect impression of the pattern than could be obtained from a starch colour *apparently* many times their thickness. Some colours are best thickened with gum, others with paste; and the colour mixer or the chemist is the only person who is sufficiently acquainted with the properties of colour materials to know exactly what to use in a given case.

Colours may, however, be suitably thickened, as far as regards material, and yet not work well in the printing machine. When this happens, the source of the trouble will usually be found to be the consistency of the colour. If too thin, it gives a slovenly, blotted impression of the design: the colour spreads out, by the capillary attraction of the cloth, beyond its proper limits, all the lines and masses of the pattern exhibit soft, spongy edges, the finer details run together, and the whole effect has an unsightly blurred appearance, due to the general lack of sharp definition.

Sometimes the blotch (background) and other large patches of colour in a printed pattern, instead of being uniform in shade, present a peculiar, irregular, mottled appearance, consisting of small spots and other variously shaped objects of light colour, distributed unevenly over the surface of the darker colour in which they occur. This particular form of unevenness is

known as " blebbing," and arises from the use of colour that is too thin for its immediate purpose. Blebbing mostly occurs with paste colours (starch, etc.), and is not always due entirely to their excessive thinness, but to that, coupled with the unsound condition of the paste itself. On standing for some time starch and other pastes break up into a curdy-looking mass, become somewhat watery, and lose their smooth, soft, gummy feel. If such pastes are let down with water to make thin colour—a procedure often adopted—they further lose what little body still remains to them, and, although they may be beaten up and strained into a seemingly smooth paste, become sloppy and quite unfit for printing. Even freshly made starch paste is apt to undergo the same transformation when diluted largely with cold water—a fact so well recognised in practice that in all well-managed colour shops extra thin paste thickenings are always specially boiled as required. The actual cause of blebbing is that, owing to the lack of viscosity or body in the colour, the roller fails to retain a sufficient supply of it to transfer a full impression of the pattern to the cloth; in other words, the thin, slushy colour slips out of the engraving before the latter comes in contact with the cloth, thus causing meagre, uneven impressions.

Colours that are too thick also produce very bare, weak impressions; not because there is any deficiency of colour in the engraving, but because it is too solid to be absorbed freely by the cloth. Delicately engraved patterns printed with *very thick* colour scarcely make a mark on the cloth, and heavy patterns, coarsely engraved, leave an impression which, instead of being full and even, lies on the surface of the cloth, and shows up nearly every line of the engraving. Both these faults are due to the same cause, namely, the inability of the colour to soak into the body of the fabric.

The remedy for printing colours that are either too thick or too thin is obvious.

(4) Frothing.—During the operation of printing, many colours are exceedingly apt to froth, especially if a brush furnisher is used in the colour box. The more a colour froths, the lighter in shade does it become and the more does it increase in bulk, so that, quite apart from causing bad work, it also causes a great deal of inconvenience by overflowing the colour box, and either flooding the floor or dropping into another colour that may be working along with it. The froth consists of a mass of minute air bubbles mixed with the colour, and is produced by the agitation which the colour undergoes in the colour box, a sort of churning action, kept up continually by the combined motions of the roller, furnisher, and doctor. The colours most liable to froth are those containing a large percentage of gum, albumen, and other elastic thickening agents, all of which, for some ill-understood reason, retain bubbles of air much more tenaciously than do starch and other pastes of a similar nature. With the exception of the acetates and formates, none of the mordants in general use is capable of forming more than a momentary froth when beaten up with air, and the same may be said of the solutions and preparations of most of the colouring matters. Pigment and lake printing colours containing soap solutions or glue-paste in addition to albumen foam up very rapidly unless they are printed at a slow speed, and even then they soon become quite unworkable if the pattern takes up too little colour to allow of the box being constantly replenished. The longer a given portion of colour remains in the box the more will it get churned up, and the sooner will it become utterly useless.

In order to reduce the tendency of certain colours to froth, it is customary in practice to add to them small quantities of benzine, pyridine, turpentine, or oil, and in the case of albumen colours, to further supplement these with a little ammonia. What rôle exactly these substances play in preventing the retention of air bubbles by gum and albumen colours has not yet been thoroughly

explained, but it is probable that they reduce the surface tension of the thickenings, and thus enable the air to escape more readily. In any case, although they are not perfect preventives, they at least preserve the colour in working condition for a considerable time, and keep down excessive frothing.

(5) "STICKING-IN" OF COLOURS.—It often happens that some portion of a colour settles in the engraving of a printing roller, and persistently refuses to leave it when the cloth is pressed into it, the result being a weak and uneven impression of the pattern. This serious defect—known as "sticking-in"—is most frequently encountered in pigment colours, Indigo, Aniline black containing insoluble salts of copper or lead, and in the numerous discharges and resists that contain china clay, zinc dust, zinc oxide, chalk, lead sulphate, and other insoluble matters; but it is also liable to occur in many printing colours which have been kept in stock too long, and in which a precipitate has been formed either by some of the constituents coming out of solution by the combination of the mordants and colouring matters, or by the reaction of the latter on the thickening. The colours most subject to spontaneous decomposition of this sort are old Alizarin colours, Basic aniline colours, Logwood and iron blacks, steam mineral colours and Catechu browns, etc.—in short, just those colours in which the colouring matters and mordants are mixed together, and especially those that contain easily dissociable compounds or mixtures which readily form more or less insoluble lakes when allowed to stand for any length of time.

The sticking-in of pigments, and the like, is generally due to faulty mixing; either the pigments are too granular, or the thickening is too thin. In either case, or both combined, the cloth only absorbs the soluble part of the colour, leaving the insoluble part in the engraving, where it accumulates until the whole is almost filled up to the level of the smooth surface of the roller. A thick colour naturally prints better than a thin, watery one, since it holds the insoluble matter in suspension better, and thus prevents it, in a great measure, from settling; but thick colours cannot always be used in pigment printing, nor are they always effective when they can, so that where sticking-in does happen with a pigment colour, the best remedy is to regrind it until it is in too fine a state of division to settle easily in its thickening. All *strong* pigment colours and others that contain, of necessity, *large* amounts of insoluble matter, are liable to stick-in, however carefully they may be made, and from all points of view they are perhaps the most difficult to print. The sticking-in may be overcome almost entirely by replacing the ordinary wooden furnisher roller in the colour box by a revolving brush; but while this keeps the engraving clear of deposited colour, and thus does away with one inconvenience, it tends unfortunately to give rise to another, namely, frothing—a defect which is, as previously pointed out, extremely likely to be developed in albumen and gum colours when a brush furnisher is used.

As regards the sticking-in of other colours, very little can be done to remedy it. Sometimes the addition of a little oil will improve matters, but usually when a mordant colour works badly from this cause it is useless, since the precipitate which ought to have been produced in the fibre of the cloth already exists in the colour. Old Basic aniline colours may be rendered workable sometimes by gently heating them with a little acetic and tartaric or citric acids, which re-dissolve the colour lake, but, as a rule, it is safer to make a fresh lot of colour, especially if it be a light shade, and cheap in consequence. Dark and expensive shades can be treated as above, and worked off little by little with newer colour. Old Alizarin reds are often mixed with Logwood black or Persian berry yellow and a little iron mordant, and then used up as dark chocolates: sometimes they work well, but usually they scum and streak badly, and cause more trouble than they are worth.

Very finely divided precipitates are often quite workable, even when they are unintentionally present in colour ; and if the lakes they consist of are only loosely combined with the mordants (that is not completely developed), they occasionally yield a colour very little, if at all, inferior in brightness and fastness to that which would have been yielded had the printing colour been in perfect condition to start with. The cloth takes up the fine precipitate, and subsequent processes complete the reaction, already started in the colour itself, converting the partially formed lake into an insoluble compound which adheres firmly to the cloth. On the other hand, however, a partly decomposed colour more often than not produces bad work, either by sticking-in, by giving a lighter shade than was intended, or by washing out of the cloth unevenly during the final soaping operations which effectually remove any loosely fixed insoluble bodies that have been transferred to the cloth along with the thickening and which become detached when the thickening is washed out. It is therefore better to avoid, as far as possible, the introduction of precipitates, however fine, into colours that are not intended to contain them, inasmuch as such precipitates cannot be relied upon to work well, and in most cases represent a dead loss of colour.

Alizarin, Anthracene brown, and other colouring matters, which are of necessity applied to the cloth in the form of finely divided powders, ground up into a paste and then thickened, often cause a good deal of trouble by sticking-in, and this can be obviated only by thoroughly sieving them through fine silk cloth before mixing them with their mordants and thickenings, and afterwards straining the made-up printing colour through the finest of " jean " cloth before sending it in to the printer. If the colour works badly after this careful preparation, the fault lies with the colouring matter itself ; some brands of Alizarin and similar pasty colours resist all efforts to strain them ; they settle into a dense, clay-like mass, which clogs the straining cloth and refuses to pass through by any means whatsoever. When this is the case it is useless to attempt to make workable printing colours of them ; the only thing to do is to return them at once to the maker,—they are absolutely unfitted for printing purposes.

Unworkable precipitates are also formed in printing colours by the irrational mixing of two or more colours to produce a compound shade. While it is true that many colouring matters and mordants, of widely diverse properties, may be and are mixed together with excellent effect, it is also true that many others mutually react upon each other, with disastrous results. If the colouring matter is not destroyed entirely, it is at least diminished in tinctorial strength, or is altered in such a way as to be incapable of proper fixation upon the cloth ; and if the mordants have been precipitated, they are liable either to stick-in or to scratch the roller. In order to avoid these accidents the most competent colour mixers utilise, as far as possible, for their compound shades, only such colours as are fixed by the same mordants, and possess a strong family likeness as regards fastness to light and washing. In this way they obtain mixtures which not only work as well as any one of their constituent colours, but which have the further advantage of behaving as a single colour when subjected to the action of soap or light—that is, they fade or wash out evenly, without undergoing any very great alteration in general tone. On the other hand, mixtures of fast and loose colours can never be depended upon to give regular results ; and as they usually belong to quite different classes of colour stuffs, they are apt also to combine with each other, forming insoluble bodies which are difficult to work ; in consequence, colours differing widely in general properties ought not to be mixed together unless the effect aimed at cannot be obtained in any other way.

From the foregoing rough outline of the generalia of colour mixing it will

be seen that, apart from all questions of correct shade and colour harmony, the technical perfection of a calico print depends very largely upon the proper preparation of the colour paste; that is to say, upon its physical nature—thickness, softness, freedom from grit, etc.,—as distinguished from its chemical composition.

With a view to avoiding the various mishaps brought about by faulty printing colours, it is usual to observe the following precautions:—

(1) All water used is examined for dirt and fine sand, and, if not free from these impurities, is filtered or allowed to settle. Condensed water should be used wherever available.

(2) Gum thickenings, especially natural gums, are allowed to settle as long as possible before use. They invariably contain fine gritty particles of one sort or another which cause damage.

(3) Starch and flour, known to contain grit and sand, or bodies that form gelatinous or flocculent precipitates on boiling, should be mixed with cold water into a thin milky fluid, and then jigged (strained or sieved by shaking) through fine straining cloth before being used for thickening purposes. Such impurities are most difficult to strain out after boiling.

(4) Pigment colours and other insoluble constituents of a printing colour must always be ground to the finest state of division possible, otherwise they are liable to stick-in.

(5) Soluble bodies ought to be completely dissolved: if colouring matters, they are also passed through a fine silk sieve into the thickening paste, so as to avoid specks.

(6) Colours thickened with dry starch or flour must be well boiled first and then thoroughly cooled before the mordants (if any) are added: neglect of these two points results in a badly working colour.

(7) When a small quantity of one colour is added to a large quantity of another it must not be thrown in bodily, but gradually diluted with successive small portions of the larger bulk, until it can be safely mixed in without any fear of its being unevenly distributed throughout the mass.

(8) All colours must be thoroughly well strained and stirred up before being given into the hands of the printer.

(9) All colour tubs, etc., must be thoroughly cleansed and well rinsed out with clean water before receiving their contents.

These simple workshop precautions appear to be considered by most writers on calico printing as insignificant details, unworthy of even passing mention, but they are none the less important on that account. They may be regarded, and justly so, as mere commonplaces of colour mixing, but at the same time their observance constitutes one of the fundamental conditions of success in all calico printing, and forms an essential part of the routine work connected with the preparation of every single printing colour. No matter how perfect a colour may be in other respects, if it be compounded without due regard to its working qualities it is practically certain to possess one or other of the defects already noted; haphazard, careless colour mixing, done in ignorance of what to expect in the way of faults, and of how to avoid them, always results, sooner or later, in bad work, damaged rollers, spoiled cloth, and a general loss of time and material.

In fine, a good colour is the *first* essential to good work, and a good colour can only be obtained by paying the utmost attention to every detail of the many consecutive operations which are involved in its preparation.[1]

[1] For information concerning the making of compound shades from ready-made standard colours reference must be made to the section on "Styles of Printing." It is impossible to give any details until the actual composition of the colours in question has been dealt with.

PART V.

TREATMENT OF GOODS AFTER PRINTING.

TREATMENT OF GOODS AFTER PRINTING.

Before proceeding to a fuller consideration of the question of colour mixing —a question to which it will be necessary to return when dealing with the practical details of the application of the various classes of colouring matters to the different styles of printing—a few general remarks on the after-treatment of printed calicoes, as compared with that of the products of an apparently similar manufacture, may not be out of place at this stage.

From the fact that the mechanical means employed for the printing of coloured designs on wall-papers and textiles is, to all intents and purposes, identical, it might be surmised that some analogy also existed between the composition and modes of fixation of the colours applied to them respectively. Such, however, is not the case: no such analogy exists or is possible; for although wall-paper is like calico in that it consists essentially of cellulose, its physical structure precludes any possibility of its being treated in the same way as a textile fabric. In fact, all resemblance between the technique of the two manufactures begins and ends with the printing of the design. Moreover, the uses to which a wall-paper is put do not require its colours to withstand the same wear and tear as those of a calico print. Without discussing this point, it may be interesting to note that in wall-paper printing a ready-formed colour (along with suitable vehicles, such as size, paste, or varnish) is applied to the surface of the paper, that it is sufficiently fixed thereon by the simple process of drying, and that it consists in its finished state of a mechanical mixture of colouring matter and vehicle or thickening; whereas in calico printing (excluding pigments) of the highest class a colour of requisite permanency or fastness can only be produced on the fibre itself by some process of local dyeing, and that a calico print in its finished state is freed, as far as possible, from all thickening matters which have been used during the printing, and which, if allowed to remain, would only impair the beauty of its colours.

With a few exceptions, the colours appearing on a piece of calico as it emerges from the drying apparatus attached to the printing machine do not exist as such, but consist of various substances, or mixtures of substances, which are capable either of attracting colouring matter from a dye bath, or of reacting upon each other, under suitable conditions, to form an insoluble colour lake. From this it is clear that the final process of wall-paper printing corresponds exactly to the initial stage in the production of a printed pattern on calico; for while a wall-paper is practically ready for the market immediately after printing and drying, a calico print in the same state requires further treatment before its colours are either developed or fixed. Of course a piece of calico can be printed in precisely the same colours as a piece of wall-paper if need be; but in that case it would not possess that quality of resisting the action of soap which has come to be looked upon as characteristic of good print, and in consequence such a procedure forms no part of the practice of calico printing, although it is true that loose work of a different kind is produced for some markets.

The object of this perhaps somewhat irrelevant comparison of wall-paper

printing and textile printing is to show (*a*) that, in general, colours of the requisite permanency cannot be obtained on textiles by the mere evaporation of a solvent or of the soluble parts of a vehicle; (*b*) that the colouring principles best suited to textile printing are those which are capable of penetrating into the fibres of the material, and of being converted therein, by chemical means, into insoluble compounds and colour lakes; and (*c*) that the development of the colour proper on textile goods is dependent upon some process of dyeing, which, whether it be performed during or after printing, must of necessity be followed by a thorough washing of the pieces, in order to remove from the *unprinted* parts all loosely adhering colour, and from the printed parts as much as possible of the thickening material used in the original printing paste.

The purpose in making this digression from the main subject of the present chapter is to point out that the printing of a design in fast colours on a textile fabric may be regarded broadly as involving two separate and distinct series of operations: the first leading up to, and completed by, the printing process; the second connected entirely with the development, fixation, and brightening of the printed colours, and with the removal from the cloth of all thickening agents, and of the dye stains, and various by-products that have been formed in the course of working. Hence, the printing process, forming, as it were, a dividing line between two quite distinct sets of operations, all work put into a piece of cloth after printing comes under the comprehensive heading of "after-treatment."

As might be expected from the immense number and diverse properties of the different colouring matters now employed in calico printing, this after-treatment varies according to the class of work in hand. Sometimes it is simple and short, sometimes long and complex, and at all times most important, especially in its earlier stages, since these cannot be repeated when once the cloth has been dyed or washed.

All after-treatments, with one or two unimportant exceptions, consist of various combinations of two or more of the following processes:—

(1) Ageing.	(5) Fixing.	(9) Soaping.
(2) Dunging.	(6) Raising.	(10) Clearing.
(3) Dyeing.	(7) Cutting.	(11) Drying, etc.
(4) Steaming.	(8) Washing.	

These several processes do not each correspond to one limited and definite mode of working, but each represents a distinct group of similar operations, which differ from each other in detail rather than in principle.

The same operation may be performed in different types of machine, and the same machines may be used equally well for widely different purposes. Such modifications as relate to the practical manipulation of the above processes will be dealt with in a general way here, but all discussion respecting the *rationale* of particular after-treatments will be deferred to a later section of this volume, in which typical examples of the more important styles of printing will be considered in detail. It would be out of place at this point to dwell on the chemistry of the subject; in fact, it is unnecessary to do so, as each style will be treated as a whole later on, and adequate reasons will be given for every step in its production. In order to avoid useless repetition, therefore, the following remarks will be confined to a general description of the principles and methods of working the above processes.

(1) AGEING.

Strictly speaking, ageing consists in exposing certain printed goods to the more or less prolonged action of a warm, moist atmosphere. Experience has

shown, however, that equally good results can be obtained in most cases by running the goods through hot steam, and, in consequence, the meaning of the term ageing has been extended to include all such improved processes.

The objects of ageing printed goods are many and various. Amongst them, the following may be mentioned as the most important:—(1) to bring about such changes in printed iron and aluminium mordants as will enable them to undergo the dyeing operation without spreading or "bleeding" into the unprinted parts of the cloth; (2) to promote the oxidation of Aniline black, Catechu brown, Manganese bronze, etc.; (3) to effect the reduction of Indigo and similar colours by one process, and their subsequent re-oxidation by another; (4) to provide the necessary conditions under which certain oxidising and reducing agents are capable of discharging the colour from those parts of an uniformly dyed fabric upon which they are printed; and (5) to assist generally in the formation and fixation upon the fibre of numerous colours and mordants which require either to be run rapidly through hot steam or to be exposed to air, under certain conditions of time, temperature, and humidity, for their proper development.

These various effects are produced by four different methods of ageing: (1) by hanging the goods in large, specially constructed ageing or hanging rooms; (2) by passing them through a continuous ageing apparatus, wherein regular conditions of temperature and moisture are maintained; (3) by a short steaming in the Mather & Platt continuous steam ager; and (4) by a recent modification of the last, in which damp steam is replaced by dry, superheated steam. Each of these systems of ageing possesses qualities which render it peculiarly adapted to certain classes of work, and therefore the choice of the particular one to employ must be guided by the requirements of the style of work under treatment.

(1) **Ageing or Hanging Rooms.**—Ageing was at one time carried out in immense brick or wooden chambers, heated at first by fire-brick or iron flues from furnaces beneath, and later by rows of steam pipes arranged underneath the grated floors. In the days when block printing was the only available means of impressing patterns on calico these chambers were known as stoves; and as it was generally believed that heat was the only factor required to convert the iron and aluminium mordants into a fit state for dyeing, no provision was made for the introduction of moisture. This is easily understood when it is remembered that the printed pieces were allowed to hang in the printing room until they were sufficiently dry to be transferred to the stoves without any fear of the colours "marking-off" or smearing. During this hanging in the printing room the processes of drying and ageing went on simultaneously; and as good results were obtained, in dyeing, after the subsequent stoving, it was only natural to infer that dry heat was all that was required to effect the necessary changes in the printed mordants. With the introduction of roller printing, however, this theory had to be abandoned. It was at once found that goods dried over steam-heated cylinders, or in hot-air machines, required several days' exposure to cool air before they could be made to take a full, deep shade in the madder dye-bath. The result was that the stoves were converted into cooling or ageing chambers by withdrawing the heat. To a great extent this was an improvement, but still irregularity in dyeing was of constant occurrence, and it was noticed that the poorest and weakest colours were always obtained during very dry or very frosty weather. The outcome was that many chemists undertook researches on the subject; but it was not until 1828 that D. Koechlin finally set at rest all doubts as to the proper conditions under which regular ageing might be ensured independent of climatic variations. In the published report of his investigations (*Bulletin de la Société*

Industrielle de Mulhouse, 1828), he not only points out that moisture, no less than heat, is an absolutely essential factor in ageing, but also that a more or less definite relationship should exist between the degrees of temperature and humidity, and that these should be kept as constant as possible during the whole operation. The temperature varies between 22° C. and 36° C., the moisture being regulated to show about 3° C. lower on the wet bulb thermometer than on the dry bulb thermometer.

In consequence of D. Koechlin's determination of the most suitable conditions under which ageing could be performed, the cooling rooms were rearranged to conform to them, and no further trouble was experienced in the production of madder-dyed work printed by machine. In these chambers, which are from 25 to 40 or more feet in height, the printed goods are hung in long loops from a series of wooden bars or rails which form a sort of secondary skeleton ceiling, between which and the roof proper sufficient space is allowed for the workmen to move about whilst hanging the cloth. The floor may be either of wood, stone, or iron grating, and the windows, doors, and roofs must all be double in order to conserve the temperature, and to avoid the condensation of the moisture in the form of drops which play havoc with the marketable value of any goods they fall upon. The necessary heat is supplied from steam pipes arranged around the base of the walls, and at frequent intervals across the floor or under the gratings; and the moisture is obtained from the same steam pipes through funnel-shaped jets, provided with taps for regulating purposes. The funnels are covered with wool or calico to prevent the accidental splashing of the pieces if the taps happen to be open too wide or the pressure of the steam increases suddenly.

The regulation of the moisture is based upon the well-known scientific fact that the closer the atmosphere approaches to the point of saturation with aqueous vapour, the more closely does the temperature registered by the wet-bulb thermometer creep up to that indicated by the ordinary dry-bulb thermometer. If, therefore, the predetermined difference between the two thermometers tends to decrease, too much moisture is present in the ageing chamber, and the steam supply must be diminished until the original conditions are restored; if, on the other hand, the mercury in the wet-bulb instrument drops, the moisture is deficient, and must be increased by opening the taps in the funnel-shaped steam jets.

The goods are allowed to hang in these chambers for from one to six days, according to circumstances. If they are simply printed in aluminium mordants, one day may be quite sufficient to age them fully; but if they also contain iron mordants or Aniline black or Catechu, a much longer time will be required as a rule, since these latter must undergo a veritable oxidation, whereas the alumina mordants only lose acetic acid. In the case of Aniline blacks developed by this method of slow ageing, it may be noted that great care should be taken to avoid exposing them to cold currents of air during the period that elapses between the time of printing and the time of hanging, cold air preventing the formation of a full shade. The exposed parts present a more or less grey appearance, and no amount of either steam or chromic acid oxidation will afterwards convert the grey parts into black.

The end and aim of ageing by hanging in a warm, humid atmosphere is to fix, as far as may be, the various colours and mordants that are used in the well-known *Madder style* of printing. A great many eminent chemists and calico printers have devoted a vast amount of time to the study of the ageing process, with a view to explaining the real nature of the chemical and physical changes that take place in mordants, etc., under the combined influence of time, temperature, and moisture. This study has been of inestimable value

to the industry, but so far has failed to supply any incontrovertible evidence as to whether the mordants, etc., are actually combined chemically with the cotton fibre, or whether they are merely fixed thereon mechanically. What is definitely known is that large quantities of acetic acid are liberated in the ageing rooms, and that the mordants are left upon the fibre in the form of insoluble basic salts; that iron mordants, *i.e.* ferrous salts, are oxidised or converted into mixtures of basic salts of uncertain composition; and that colours capable of absorbing atmospheric oxygen do so in varying degrees, according to the length of time they remain in the chamber. Apart from the temperature and moisture of the atmosphere of the ageing room, the amount of acetic acid and other vapours present exercises a considerable influence upon the speed and effectiveness of the ageing. It stands to reason that if the chamber is overcharged with free acetic acid vapour its efficiency will be reduced, by reason of the fact that the evolution of the acid still retained as acetate by the mordants on the cloth will be retarded, if not prevented altogether; and further, if heavy patterns, printed with strong iron mordants, are hung in a closed chamber, they rapidly absorb all the available oxygen, or at least most of it, before they are sufficiently aged, with the result that irregular work is produced. The same obtains with such colours as Aniline black and Catechu brown when used in conjunction with mordants for madder colours. The remedy for these disadvantages is obvious, viz. ventilation. This can be obtained either by fixing suitable hoods in the roof of the chamber, or, better, by blowing-in a mixture of fresh warm air and steam through a fan, the old air and acid vapours being thus driven out through any conveniently arranged flue or hood. The introduction of a constant current of fresh air and steam into an ageing chamber filled with cloth requires very careful management to avoid causing sudden changes of temperature, and is only successful when carried out without giving rise to any appreciable fluctuations of heat and humidity. Given a sufficiently spacious chamber, provided with doors, windows, and a few ventilators in the roof, and the ageing ought to proceed in a regular manner, without the necessity of an artificial draught; in fact, very few ageing rooms in England are fitted up with any such appliance.

Where ageing rooms still exist, they are used to advantage; but to a great extent they have been superseded by a modification of Thom's Continuous Ager, and in many works they have been put to other uses, being transformed into ordinary departments by the addition of intermediate floors, etc.

(2) **Thom's Patent Ageing Chamber.**—To John Thom, of Mayfield, belongs the credit of having first devised a machine for the continuous ageing of mordants printed on cotton cloth. For this purpose it was necessary that the moisture should be introduced into the apparatus in a systematic manner, and that all excess of acid vapours, etc., should be enabled to escape. These conditions were successfully fulfilled in Thom's patented machine (Eng. Pat. 22610, 1849), a sketch of which is shown in fig. 57.

The ageing chamber, A, A, consists of a wooden cottage with gable ends, the roof being pitched at an angle of 45°. Inside, it is furnished with top and bottom guide rollers R, R, over and under which the goods are drawn. Beneath the chamber a stone cistern C is situated in the brickwork foundation. This cistern is partly filled with water into which a steam pipe S dips, and is provided with an overflow pipe O, so as to maintain the level of the water. Immediately above the water, a double series of planks P, P are so arranged that the upper ones come over the spaces between the lower ones, and thus prevent any chance of the cloth getting splashed when the water is heated by the steam entering through the pipe S. Ventilation is obtained by means of the outlet pipe E fixed at the peak of the gable. The cloth K to be aged enters and leaves the

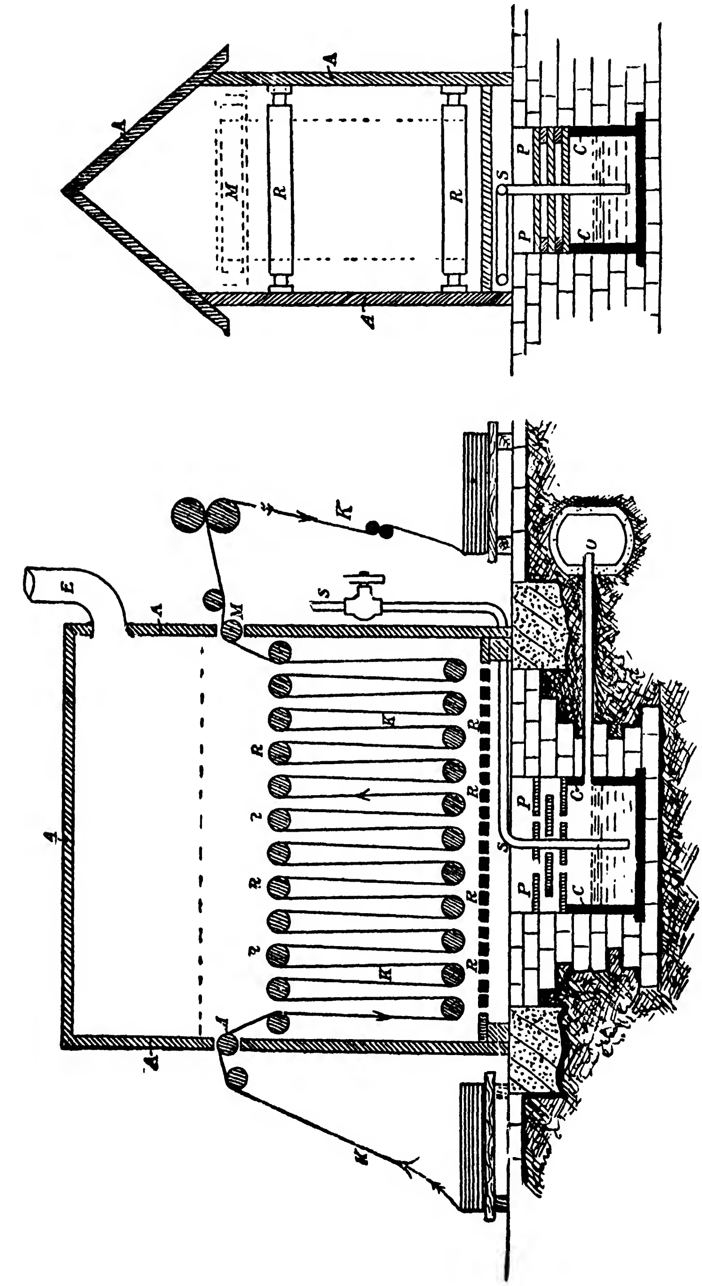


FIG. 57.—Thom's ageing machine.

chamber over the woollen-covered rollers M, M, situated in slits cut in each end of the chamber. In operation the water in the cistern is heated to 180° F., at which temperature it gives off aqueous vapour; this gradually fills the chamber above by escaping between the planks P, P, and when the requisite temperature is attained the goods are passed through slowly, and, on emerging, are either plaited down or bundled up loosely. In either case they are allowed to lie about, a day or two, in pile in the room where the ageing machine is situated, and in which is maintained a suitable degree of heat and humidity. Goods treated in this way may sometimes be sent forward to the dye-house at once, but, as a rule, it is preferable to let them age for a day or two in pile before dyeing. The piles are turned over once or twice to equalise the ageing.

Walter Crum, of Thornliebank, adopted Thom's principle of continuous working, but enlarged the chamber and introduced the same system of heating and supplying moisture as is used in the old-fashioned hanging rooms already described. By this means he was enabled to deal with a much larger quantity of cloth at a time, and, in addition to obtaining more satisfactory results, he effected (as Thom did also) a considerable saving of valuable floor space, since goods in bundle or in pile take up much less room than when suspended from bars in single folds.

A diagram of a machine based upon Crum's improvements is given in fig. 58.

In Crum's original machine the chamber was of wood, but in the instance given (fig. 58) it consists of a brick room 40 feet long, 24 feet high, and 17½ feet wide. It is situated inside the works, an advantage which cannot be over-estimated when condensation of moisture is in question. The width allows of three widths of ordinary cloth being treated at one time; and as most madder work is done on 30″ material, the space allowed is more than ample. If need be, broader cloth can easily be run; but if it exceeds the length of the guide rollers these will require to be replaced with wider ones—a simple matter if broad work is a regular article of production. Three separate sets of top and bottom rollers R, R are installed; and heat and moisture are obtained from the steam pipes S, S, and the cloth-covered funnels F, F, respectively. In other respects the working of the apparatus is identical with Thom's, except that the cloth is arranged to emerge on the entrance side. For the purpose of preventing the formation of drops, the ingress and egress slits are furnished with copper steam pipes C, C, between which the cloth passes over the rollers M, M. The fumes disengaged during the operation are drawn off by a small fan, B through the exhausts A, A, A; the fan only works when required, or it may be allowed to revolve slowly and continuously if unusually large amounts of acid are given off from heavy patterns printed in strong mordants. According to the class of work under treatment, the temperature of the ageing chamber varies from 25° C. to 36° C., with a constant difference of about 3 degrees between the indications of the wet- and dry-bulb thermometers. The time occupied by the pieces in passing through the chamber depends upon the nature of the mordants and the weight of thickening in the printed parts of the cloth. Strong mordants, somewhat basic in character, require less time to age than weaker mordants, to which extra acetic acid has been added to overcome their liability to dissociate; and fine patterns printed from lightly engraved rollers absorb the moisture more rapidly than heavy patterns printed from deep engraving, which deposits a much larger quantity of thickening on the fibre. This thickening presents a hard, dry surface to the air, and prevents the moisture from reaching the fibres of the cloth unless sufficient time is allowed for it to become softened in the moist atmosphere of the ageing chamber. For the majority of madder styles the goods are run at such a speed as to be 18 or 20 minutes in passing

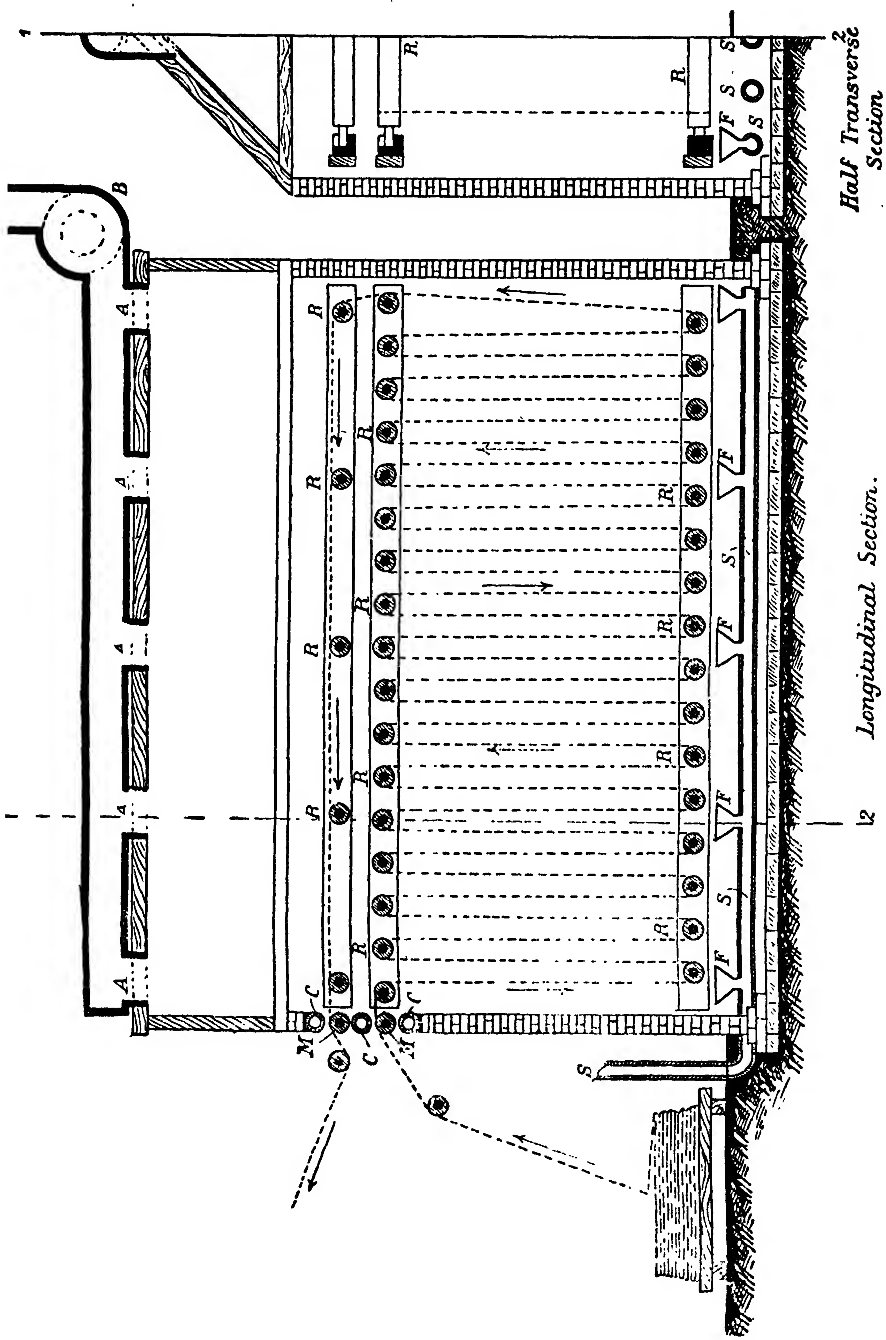


Fig. 58.—Crum's ageing machine.

through the chamber, but in special cases the time may be increased to 35 minutes.

As a rule, if the goods are found to contain 6 per cent. to 7 per cent. of moisture, evenly distributed throughout, they may be regarded as having been sufficiently aged, that is, if they were quite dry to start with. On leaving the chamber the goods are plaited down, and allowed to lie a day or so before dyeing. Iron mordants ought always to lie three to four days in a warm, moist atmosphere after ageing, in order to enable them to absorb as much oxygen from the air as they are capable of taking up, otherwise they exist on the piece in various states of oxidation, and dye up unevenly in consequence. The only real drawback to Thom's system of ageing is that Catechu browns printed along with iron and aluminium mordants cannot be fully oxidised by so short an exposure to the atmosphere of the ageing chamber. In all other kinds of madder-dyed work this exposure is sufficient to carry the *ageing* to a point from which it proceeds to completion by natural means during the time that the goods are stored in bundle previous to dyeing; but in the case of Catechu the colour can only be fully developed by a rather prolonged exposure to freely circulating, warm, moist air, and for this reason it is preferable to hang goods printed with Catechu in single folds in one of the old-fashioned ageing rooms for four or five days. However, at the present time this one drawback is not of much moment, since Catechu and madder-colour effects can be easily and successfully matched in other ways that give equally good results. Before leaving the subject of ageing chambers it may be remarked that the atmosphere of the rooms in which they are situated, and in which the goods are stored after passing through the chamber, ought to be maintained in a condition corresponding, as near as possible, to 24° C. dry-bulb and 21° C. wet-bulb thermometers.

(3) **Mather & Platt's Rapid Steam Ager.**—This machine, known throughout the calico-printing world as the "Mather-Platt," was brought out in 1879, and at once achieved a well-merited and lasting success; so much so, in fact, that it is now an indispensable piece of plant in all modern printworks.

The original model, of which many examples are still in use, consists of a comparatively small iron chamber, inside which top and bottom rollers are fitted. The top of the chamber consists of a wooden hood, arranged to carry off the gases disengaged during the operation of ageing. A pipe from the top of the ager runs into this hood, the ventilating shaft of which communicates with the outer air; and the ventilation required may be obtained either by the current so induced or by means of a fan working in the shaft itself. The cloth enters and leaves the machine through the same aperture, which is provided with two steam pipes, fixed longitudinally, to prevent drops of condensed water forming and falling on the cloth (see fig. 59).

The apparatus is supplied with low-pressure steam through a perforated pipe situated beneath the lower set of guide rollers. Where a steam engine is used for driving, its exhaust steam may be utilised for this purpose; but in general better results are obtained from a special supply pipe, which can, of course, be used to keep the chamber in working condition whilst the engine is stopped. Any condensed water formed runs down the sides of the chamber, and is drawn off by a syphon situated at the bottom. If the apparatus occupies a position in which it is exposed to cold draughts, it is usually boarded round in order to keep it hot, thus avoiding an undue condensation of the steam.

The great variety of purposes to which the rapid ager is adapted, combined with its high rate of production, has enabled it to take the place of both the preceding forms of ageing in all cases where rapidity of oxidation is not detrimental. For madder styles it is not so well adapted as are the older

and slower methods, but, all the same, large quantities of this style are produced by its means, especially if they contain Aniline black; and if proper precautions be observed, the final results leave little to be desired. Aniline blacks,

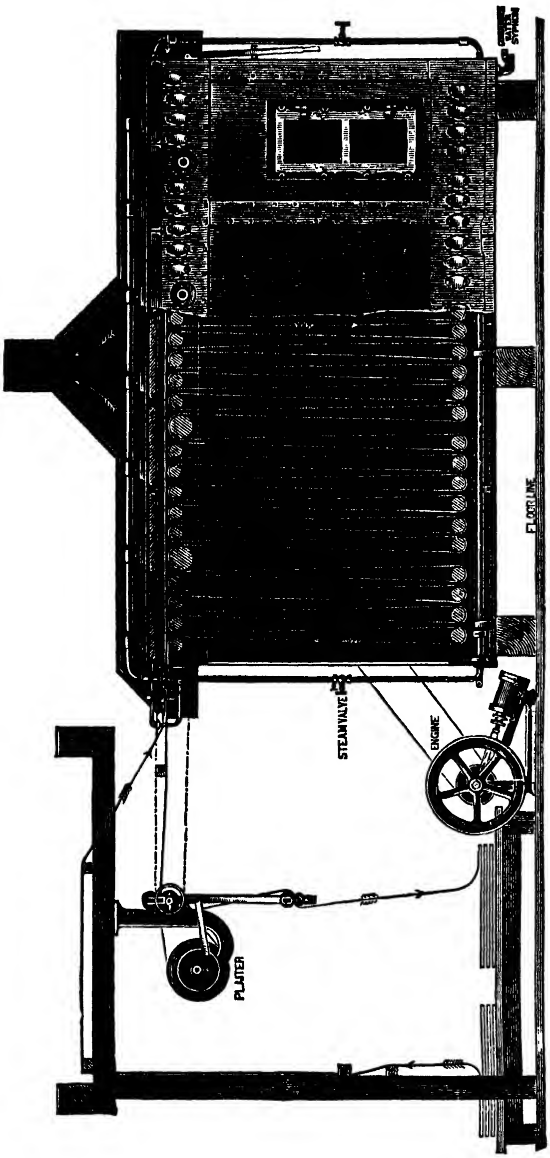


FIG. 59.—Mather & Platt's rapid steam ager (original model).

which formerly took at least six hours to oxidise in the hanging rooms, can be fully developed in the rapid ager in half the number of minutes; and styles such as the printing of Indigo by the Schlieper & Baum process, the alkaline discharge of Turkey-red and tannin mordants, and many other discharges, both by oxidation and reduction, all of which were impossible under any conditions previous to the invention of the rapid ager, can now, by its means, be produced with ease and certainty. So that, quite apart from the great

advantage it has in increasing the output, the rapid ager has been instrumental also in increasing the resources of the textile colourist by rendering possible the practical application of many processes that were previously of scientific interest only.

The temperature at which the Mather & Platt steam ager is worked varies from 65° C. to 95° C. with the dampness of the steam regulated to show 3° C. less on the wet-bulb thermometer. The lower temperature is employed for Vanadium and Copper aniline blacks, either alone or in combination with iron and aluminium mordants, and the higher temperature for Prussiate blacks in all styles. The Prussiate black will stand still greater heat than 95° C., but without exhibiting any improvement in shade. The goods are usually run at a speed of 60 yards per minute, and at this speed take 3 minutes to pass through the chamber.

From a practical colourist's point of view, the rapid ager has two great advantages over all other systems of ageing. In the first place, it permits of the important Prud'homme style of Aniline black discharging being produced to the utmost degree of perfection; and secondly, it allows of Indigo and other vat dyes being reduced on the fibre in presence of caustic soda. Neither of these processes can be carried out in any other apparatus or by any other means. If Prud'homme blacks printed in coloured discharges are hung, the black is poor and the colours are dull; and all processes in which caustic soda, as such, plays an important part must, of necessity, be completed before the caustic has time to become converted into carbonate, by the absorption of carbonic acid from the air.

When the rapid ager was first introduced for the oxidation of Aniline blacks and other printing colours containing free mineral acids, a good deal of trouble was experienced from the extreme liability of the cloth to become tender. This defect was found to be caused not by any inherent defect in the machine, but by the too great percentage of acid in the colours themselves. In the hanging rooms these same colours came out very well, but when subjected to the energetic oxidising action of the rapid ager the free acid liberated rapidly destroyed the cloth at the temperature at which the operation was performed. A modification of the composition of the printing colours was all that was required to remedy the defect, and nowadays, when tendering of the cloth occurs, it may safely be attributed to one of three causes:—(1) the acidity of the colour; (2) too great a heat in the ager; and (3) to the goods being allowed to stay too long inside—that is, not passing through the ager quickly enough. If these three points are attended to, the Mather-Platt rapid ageing and steaming chamber will be found to give perfectly reliable results, and to possess all the many advantages claimed for it.

(4) **Ageing with Superheated Steam.**—The only reason for including this system under the heading of Ageing is that it is carried out in a chamber that is, to all intents and purposes, an obvious modification of the ordinary rapid ager.

The powerful reducing properties of the solid sulphoxylate-formaldehyde compounds or hydrosulphites, employed in the printing of vat colours and discharge styles, can be utilised to the best advantage only when the goods upon which they are intended to act are exposed to the action of high temperature air-free steam. For this purpose the ordinary rapid ager just described is unsuited and, in consequence, it became necessary to modify its construction and arrangements. The result of numerous experiments is that many types of "hydrosulphite ager" are now on the market—all more or less efficient. Amongst these the most generally useful perhaps is the combined *Hydrosulphite and Aniline Black Ageing Machine,* made by Messrs Mather & Platt,

Ltd., of Manchester. This exceedingly efficient and convenient machine fulfils all the conditions essential to the successful production of the various hydrosulphite styles, namely, a high working temperature, the least possible admission of air, and an arrangement for supplying the moisture that is necessary in the steaming of Indigo and vat-dye prints. It is also easily adapted for Aniline black styles of all descriptions, and for the ageing of mordants, without the slightest trouble.

As shown in figs. 60 and 61, the walls of the chamber consist of flanged iron plates, accurately machined on their edges so as to fit together perfectly

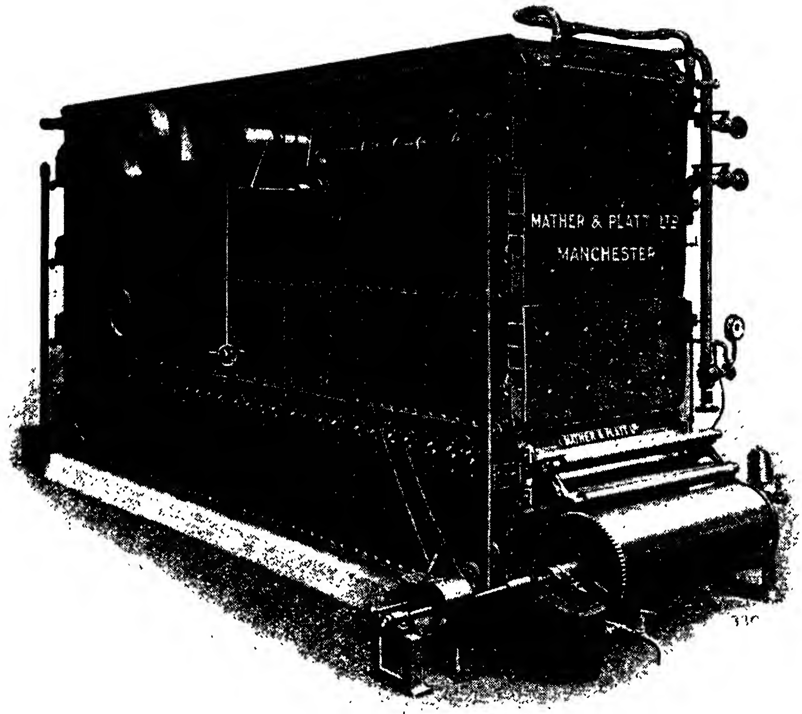


FIG. 60.—Hydrosulphite-Aniline ager.

air-tight. The fixings carrying the rollers are machined on their faces, and are fitted to machined facings on the side plates, so that the rollers run truly and freely. The roof of the chamber is made up of cast-iron steam chests, which, in conjunction with a closed high-pressure steam coil in the bottom of the ager, serve to maintain the chamber at the temperature requisite for hydrosulphite work, viz. about 104° C. All the guide rollers are made of seamless drawn copper tubes running in bearings bushed with bronze and provided with "Stauffer" lubricators, which allow of them being lubricated from the outside whilst the machine is running—a great convenience. The steam supply to the interior of the ager enters through two perforated pipes running along the length of the upper part of the chamber—one on each side—and before entering it passes through a separator or steam trap, where any water it may contain is removed. Each perforated supply pipe is enclosed in an outer

perforated pipe, which, as the two series of perforations are arranged not to coincide, serves as a guard to prevent any possibility of the cloth being damaged by drops and splashes. Two similar pipes are situated at the bottom of the ager to supplement the steam supply of the upper pipes.

The bottom of the ager forms a tank in which the water condensed in other parts of the machine is collected. This water, according to circumstances, is either syphoned-off continuously or retained. If retained, the supply is augmented by condensed water collected from the outlet of the closed heating coil or other source, the coil being utilised for boiling this water and thus generating the damp steam that is necessary for the reduction of Indigo and other vat dyestuffs.

The cloth enters and leaves the machine through a steam-heated mouth-piece provided with an automatic closing device which, whilst preventing almost entirely the entrance of air, allows of both air and steam being emitted, thus maintaining an atmosphere of air-free steam inside the chamber.

As cold damp cloth passing into the chamber would reduce its efficiency, the goods to be aged are passed round a steam-heated drying cylinder before entering

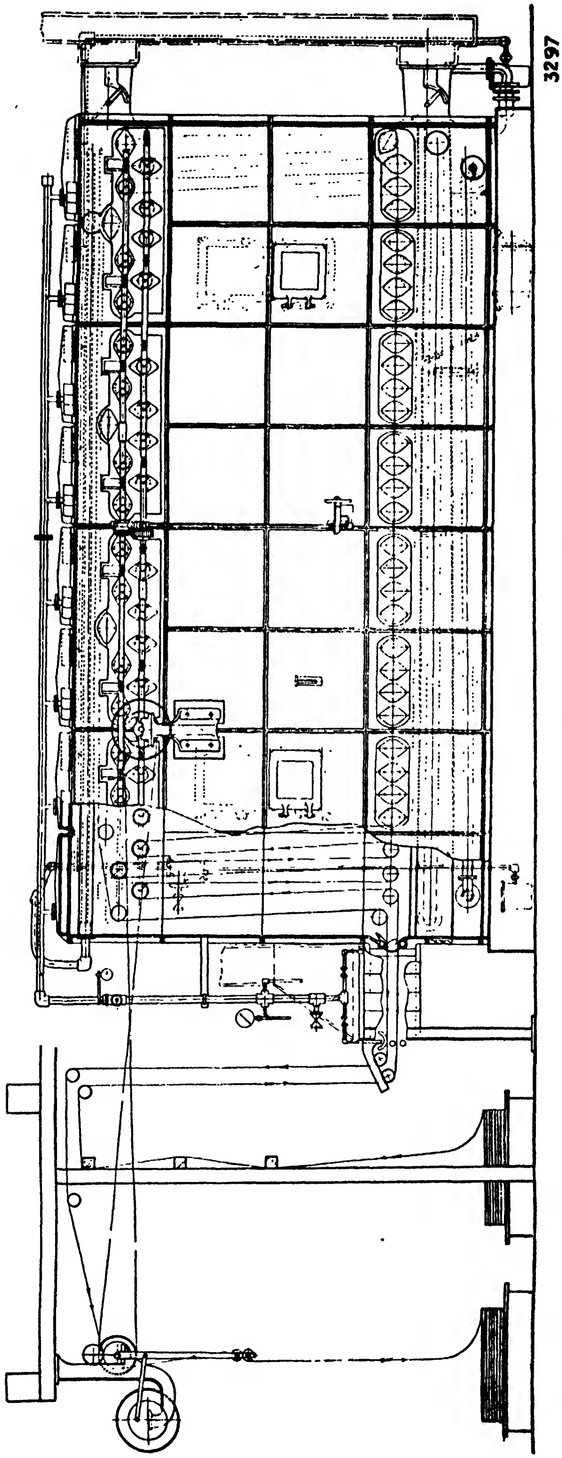


Fig. 61.—Ageing machine for vat colours.

the mouthpiece of the machine (see fig. 60). All undue tension on the cloth whilst travelling through the machine is avoided by driving the top rollers, through bevel wheels, by means of side shafts geared together; and, if desired, the undriven bottom rollers may be provided with ball bearings.

Ventilation of the chamber, in so far as it consists in removing the gases disengaged during the operation of ageing, is secured by means of two butterfly wing ventilators fitted to the back end of the chamber, and connected through any suitable trunk with an exhaust fan. These ventilators are used when steaming Aniline blacks, chlorate discharges, and similar styles.

Every precaution is taken to avoid the troubles due to condensation—drops and splashes of water. Gutters are provided inside the ager, and copper flashings under the observation windows and doors, to collect the condensed water, which is drained through copper pipes to the bottom of the ager. A copper

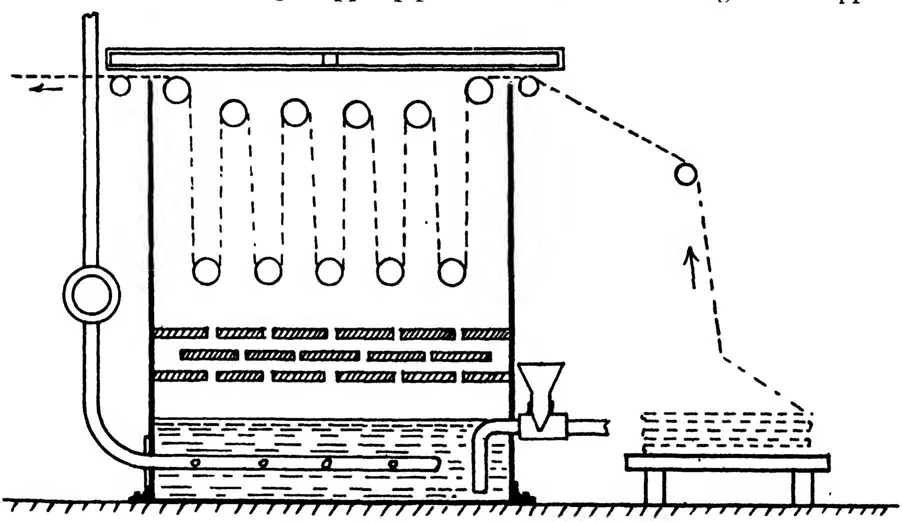


FIG. 62.—Indigo (glucose-alkali) ager.

gauze sheeting extends over the entire area of the bottom of the ager, slightly above the steam heating coil, and serves the twofold purpose of preventing violent ebullition and of ensuring complete saturation of the steam when the coil is used for generating saturated steam. The perforated steam supply pipes at the bottom of the ager are also covered by a perforated double false bottom in order to minimise the danger of splashes and drops.

If desired, the machine can be arranged for the steaming of two superposed pieces of cloth simultaneously, thus doubling the output of certain styles of work.

Superheated steam agers are indispensable in all works where processes depending on the reducing action of the hydrosulphite-formaldehyde compounds are in use. The discharging of certain Azoic colours cannot be effected in any other apparatus, but Indigo may be reduced by hydrosulphite in the ordinary type of rapid ager if care be taken to keep the temperature up and to avoid the presence of too much moisture. On the other hand, the glucose process of Indigo printing absolutely requires the presence of moisture, and therefore cannot be carried out in superheated steam agers unless they are specially adapted to its requirements.

(5) **Indigo Ager** (for the glucose process).—The ordinary ager used for this

process is much simpler in construction than the combined hydrosulphite, Aniline black, and Indigo ager just described ; it resembles in some respects Thom's ageing machine, the main differences being in its smaller size, in the chamber being filled with steam as free as possible from air, and in the passage of the cloth being reduced from about 20 minutes or more to from ½ to 2 minutes only. A glance at fig. 62 will show clearly the arrangement of a special Indigo ager for the glucose process.

The chamber itself is made of iron plates ; the lower part is arranged to serve as a cistern ; and the roof, as in all the best modern agers, is composed of cast-iron steam chests, the heat of which precludes any possibility of drops of condensed water forming on its under side, and dropping therefrom on to the pieces passing through beneath. The steam enters the chamber through the water in the cistern, and thus becomes charged with the necessary moisture. Above the cistern an arrangement of overlapping plates is provided to prevent the cloth from getting splashed by the boiling of the water below ; suitable precautions also are taken to avoid drops of water condensing on the edges of the slits through which the goods enter and leave the chamber.

This apparatus ensures the rapid and even reduction of Indigo ; and although it is not absolutely essential to success, it is perhaps the safest system to adopt for the purpose. In many works the ordinary ager can be made to yield equally good results if properly handled and supplied with damp steam ; in fact, many firms who print Indigo by the Schlieper & Baum process make no other arrangement for its steaming beyond providing for the introduction of plenty of moist steam into any type of ager they may happen to have in use.

(2) DUNGING.

Dunging is an operation specially connected with the after-treatment of goods printed in iron and aluminium mordants, and derives its name from the fact that cow-dung enters largely into the composition of many dunging liquors. It consists in passing the aged cloth through cow-dung let down with water or through a solution of cow-dung substitutes, and occasionally, for delicate work, through a bath of bran and chalk. Dunging constitutes one of the most important steps in the production of the madder style, and demands the utmost care in its performance, since upon the state of the cloth as it leaves the final dunging beck depends the ultimate success of the work.

The function of dunging may be described as threefold, namely, (1) to complete the fixing (already partly accomplished in the ageing chamber) of the mordants on the cloth ; (2) to combine with and render insoluble any undecomposed mordant that may dissolve out of the cloth as it passes through the liquor ; and (3) to remove, as perfectly as may be, all the thickening material used in the printing colour ; in short, its function is to prepare the printed cloth in such a manner as to enable it to take up evenly the requisite quantity of colouring matter from the dye bath.

The necessity for dunging is almost too self-evident to call for explanation. However, it may be noted that if cloth plastered with thickening and containing unfixed mordants were entered into a dye bath, the thickening, by acting as a mechanical resist, would prevent the dyestuff from penetrating into the fibres of the material, and thus give rise to irregular dyeing ; and the unfixed mordants would dissolve off in the hot dye liquor, and not only cause uneven dyeing, but also attach themselves and attract colour to the white unprinted portions of the cloth, thereby staining them beyond remedy. Besides, the presence of soluble mordants in a madder dye bath is productive of great loss of dyestuff : the mordant combines with the colouring matter to form insoluble lakes, which

simply float about in the dye liquor, only to be thrown away after spoiling the goods. Imperfectly dunged goods are subject to these same mishaps in a less degree, so that, from all points of view, the thorough cleansing (dunging) of printed goods from all foreign matters, other than those that go to form part of the ultimate colour, is an operation of extreme importance.

The use of cow-dung as a cleansing agent is the outcome of practical experience alone. The nature of the chemical and physical changes that take place in the dunging process has never yet been ascertained definitely. All that is known is that it fixes the greater part of the mordant which has already been partially converted into an insoluble basic salt by the action of the ageing process; that it prevents the unprinted parts of the cloth from becoming mordanted, and thus subsequently attracting colouring matter from the dye bath; and that it removes effectually all thickening agents, leaving the cloth in the best possible state for being dyed up fully and evenly. Fresh cow-dung is slightly alkaline, and contains, besides water and some phosphates, a fair percentage of albumen and a considerable amount of insoluble organic matter. The alkali and albumen both precipitate iron and aluminium mordants, and the insoluble matter also has a powerful attraction for them, so that any mordant that may dissolve out of the cloth immediately enters into combination with them, and, in being thus rendered insoluble, is prevented from injuriously affecting the unprinted parts of the cloth—the "whites."

Although cow-dung is generally acknowledged by practical men to be superior to any other dunging agent, it requires careful application to secure the best results. An excess impoverishes and dulls the colours, and imparts an unpleasant greenish tinge to the whites. It also varies considerably in composition; and in working requires to be emptied out and thrown away at frequent intervals, by reason of the large amount of thick sediment formed, which, if allowed to act upon the goods, would inevitably ruin the whites. As a rule, one charge of cow-dung cannot be used for more than 200-300 pieces of calico without causing trouble.

With a view to overcoming the disadvantages of cow-dung, many substances have been suggested as dung substitutes. Amongst them the most commonly used and most important are the following:—

(1) Sodium Phosphate ($Na_2HPO_4.12H_2O$).—This salt is extremely useful for the fixing of mordants that are too delicate to stand the energetic action of cow-dung, and in cases where a weak mordant is printed in combination with a strong one, *e.g.* the red and pink madder style.

(2) Sodium Binarsenate ($Na_2HAsO_4.12H_2O$).—This salt, known as arsenate, is perhaps used more than any other as a dung substitute in England. It acts like sodium phosphate in all respects, and in countries where it is not prohibited it is generally preferred on account of its greater efficiency. The poisonous nature of goods dunged with binarsenate is very much exaggerated. As a matter of fact, the salt is either removed from the cloth during the many subsequent washings it undergoes, or is combined with the mordant and colouring matter in an insoluble and quite innocuous form. The only danger to be apprehended from its employment is, that it may possibly contaminate the stream into which the effluent of the works runs; but nowadays this danger is reduced to vanishing point, since most river and canal authorities insist upon all poisonous substances being eliminated from the effluent before it leaves the works. A good sample of binarsenate of soda ought to contain at least 50 per cent. of the pure salt.

(3) Silicate of Soda ($Na_2Si_4O_9$).—This salt occurs in the solid form as "soluble glass," but it usually comes into commerce as a thick, colourless, syrupy liquid. It finds but limited use as a dunging agent, on account of its

liability to contain an excess of either caustic soda or carbonate of soda, both of which strip aluminium mordants from the cloth at the temperature of the dunging bath. Basic salts of aluminium readily dissolve in warm alkali, and in consequence the use of silicate of soda is attended by some risk, especially if applied to the red and pink style. On the other hand, iron and chromium mordants, not being soluble in weak alkalies, can be fixed in silicate with safety. Although freshly and properly prepared silicate of soda is not open to the above objections, it nevertheless decomposes into silicic acid and a basic salt if kept long in solution. The main drawback to the use of silicate, however, is that aluminium mordants fixed by its means yield poor and dull shades of red when dyed up in Alizarin.

(4) Sodium Carbonate ($Na_2CO_3.10H_2O$) and "crystal carbonate" ($Na_2CO_3.H_2O$) are only used for the fixation of iron and chromium mordants in certain cases.

(5) Ammonium Carbonate [$(NH_4)HCO_3.(NH_4)CO_2.(NH_2)$] in the dry state is a mixture of the bicarbonate and carbamate, but when dissolved in water and ammonia it is converted into the normal carbonate $(NH_4)_2CO_3$. It is an excellent dunging agent for aluminium mordants, but hitherto has not found much employment on the large scale, probably on account of its price.

(6) Silicate of Lime, recommended by Higgin as a cow-dung substitute, is little used. It is a sparingly soluble salt, which is employed as a saturated solution, the strength of the bath being kept up by always allowing an excess to remain in suspension in the dunging liquor.

(7) Bran. This substance cannot be regarded as a dung substitute proper, although it is frequently used along with a little chalk for treating weak aluminium mordants which are so far fixed upon the fibre in ageing as not to require a more drastic treatment. The diastase ferment in the bran converts the starchy matters in the thickenings into soluble glucose, which easily washes out of the cloth, while the chalk serves to neutralise any traces of acid that still remain after the ageing process. Chalk is a regular constituent of all dunging liquors; it combines with all acids liberated by the dunging agents, and acts generally as a weak and useful, though harmless, alkali.

The advantages accruing from the use of dung substitutes lie in the direction of increased cleanliness, convenience, and regularity of working, rather than in the better fixation of the mordants or the more perfect removal of thickening materials. Dung substitutes effect neither of the latter two objects any better than cow-dung, if as well; but being colourless, regular in composition, and, with the exception of bran and chalk, quite soluble, they neither stain the cloth, give rise to irregularities in shade, nor require to be thrown away every few hours, as is the case with cow-dung. A dunging machine set with sodium phosphate, etc., can be worked a whole day without emptying out, whereas with cow-dung a considerable amount of time is lost owing to the necessity for emptying out and re-charging the machine with fresh cow-dung at frequent intervals, the length of which varies according to the class of work under treatment. Heavy patterns require fresh liquor oftener than light patterns, and the kind of thickening used also governs the working of the dunging process to some extent, since starch and flour are more difficult to remove than the various gums.

A dunging liquor made up from any of the foregoing substitutes may often be used continuously for several days if it be replenished regularly with a little fresh solution. The amount to be added is easily calculated when it is borne in mind that the cloth usually abstracts its own weight of solution from the bath: the bath, however, should be kept as much as possible at the same height during the whole time of the operation, and therefore it is advisable

not to allow too many pieces to pass through it before freshening it up with a few gallons of new dunging liquor from the storage cask kept conveniently at hand.

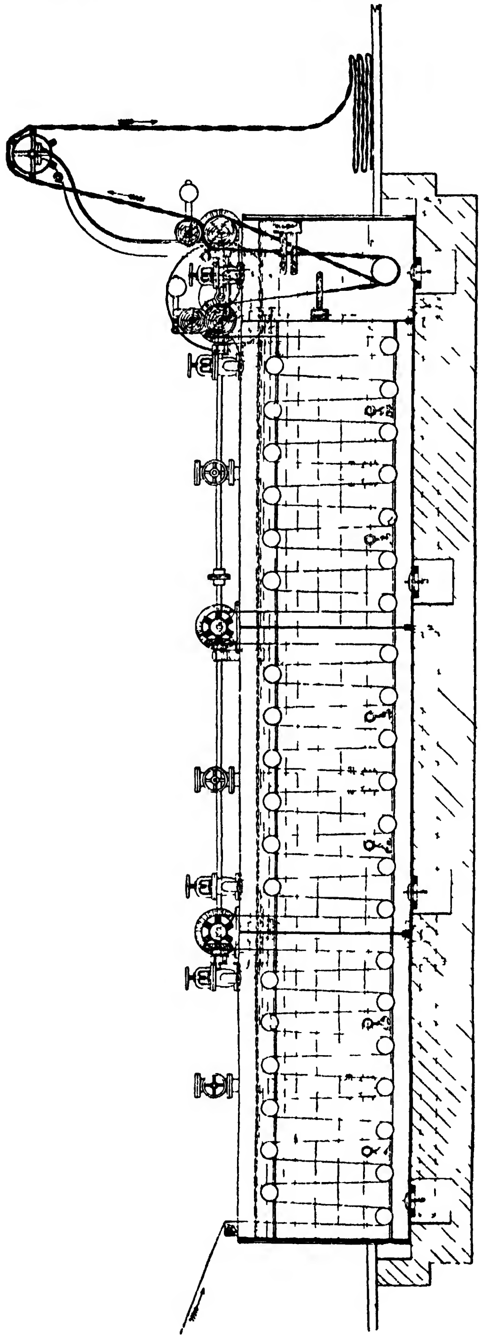
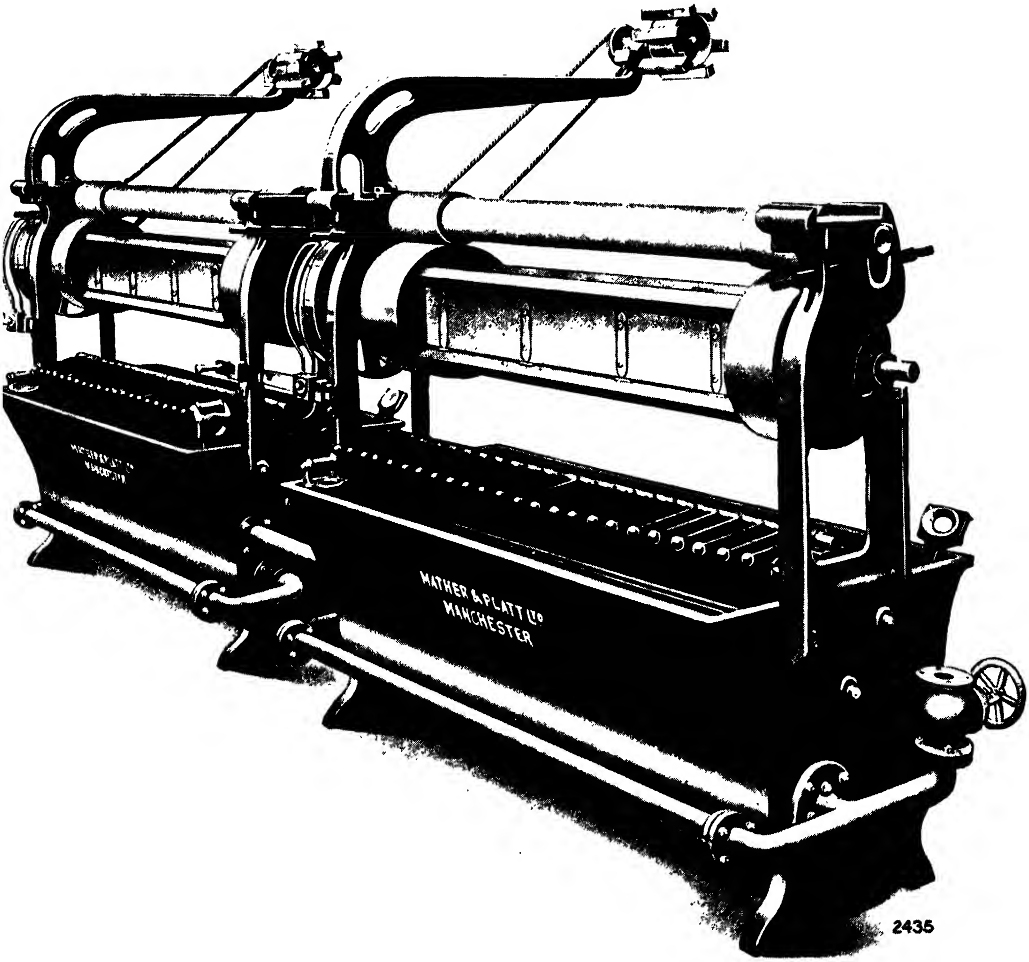


Fig. 63.—"Fly" or first dunging becks (Mather & Platt).

Most of the dunging substitutes in common use can be mixed in any proportion either with each other or with cow-dung. Indeed, cow-dung, phosphate of soda, and chalk is a very general mixture for the first dunging of ordinary madder styles, the second dunging consisting sometimes of phosphate alone, and sometimes of a dilute solution of cow-dung and one or other of its above substitutes, together with a little chalk or bran.

As a rule, it is essential to dung all madder styles twice at least in order to ensure the perfect removal of the thickenings used in printing the mordants. The first dunging is known as fly dunging, and is performed in a series of three or more becks, through which the cloth passes, in the open width, over a system of rollers. The second dunging is carried out in one of the many types of spiral washing or dyeing machines, and the goods are, of course, treated in the rope form.

In fig. 63, which represents a section of Mather & Platt's fly dunging machine, the first compartment is filled with the required liquor at a strength a little above that of the similar contents of the second and third compartments. This difference in strength is not absolutely necessary, but it is found to give the best results in many works. The cloth enters as shown, passes through each beck in succession, and in the last or washing beck is drawn through an earthenware ring or "pot eye," which throws it out of the open width into the rope form, in which form it



Second Dunging Becks.

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proceeds to the second dunging. The temperature of the dunging liquor varies from 60° to 100° C. according to circumstances that will be mentioned later. The usual duration of the first dunging is from 2 to 5 minutes.

The second dunging occupies 20 to 30 minutes at 60° to 65° C. It is performed in a spiral machine, similar to dyeing and washing machines, and sometimes two machines are run in combination, the goods passing from one to the other in a continuous manner (see Plate VIII.). On emerging from the second dunging the pieces must be thoroughly washed, and are then ready for dyeing.

Fig. 64 will give an idea of the working of a spiral dung beck.

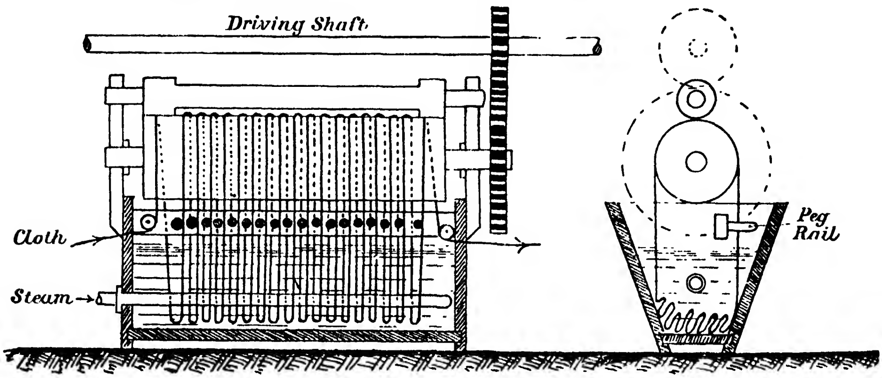


FIG. 64.—Spiral or second dunging becks.

(3) DYEING.

The dyeing of printed calico, either before or after printing, is performed in at least four distinct ways, each of which may be modified according to circumstances.

For dyeing in the *open width,* use is made (1) of jiggers, (2) of continuous dyeing machines constructed on the same principle as the fly dung becks (see fig. 63), and (3) of slop-padding mangles (see figs. 55 and 56).

In the *rope form,* cloth is nowadays invariably dyed in spiral dye becks, of which various types exist.

Fig. 65 shows a section of the jigger, a machine largely used for dyeing plain shades, but which does not find very extensive employment in printworks where the output is confined to printed goods. It may, however, be used with advantage for small quantities of certain discharge styles, such as the alkaline discharge on tannin-mordanted cloth. In this style, when the same design is required in small lots of different colours, the jigger affords an economical means of dyeing the comparatively short lengths into which the order is split up.

The jigger consists of an iron or wooden dye beck fixed between two cast-iron supports, which carry bearings in which two fixed rollers revolve. To each bearing an oblique arm is attached for the purpose of supporting a loose roller in such a way that it is capable of revolving in contact with the fixed rollers. The goods to be dyed are sewn end to end and wound on a loose shell, which is then placed upon one of the arms. The goods are now threaded by hand under and over the guide rollers immersed in the dye liquor until sufficient has been pulled through to be wound on the fixed roller at the opposite side of the jigger. The machine is then set in motion, and as soon as the whole length of cloth has passed through the dye liquor the motion is

reversed, so that the pieces pass back again and are wound on the opposite fixed roller. These to-and-fro passages are continued until the cloth is fully dyed, at which point, *i.e.* during the last passage, they are wound on a second loose shell instead of on a fixed roller. The dye liquor may then be replaced, if desired, by water, and the goods washed in exactly the same way. In some machines the reversing motion takes place automatically. Jiggers are driven by bevel gearing, acting directly on the axles of both the fixed rollers; and their contents are heated by either open steam pipes or by steam coils situated beneath the guide rollers.

The working of slop-padding machines has already been described, and that

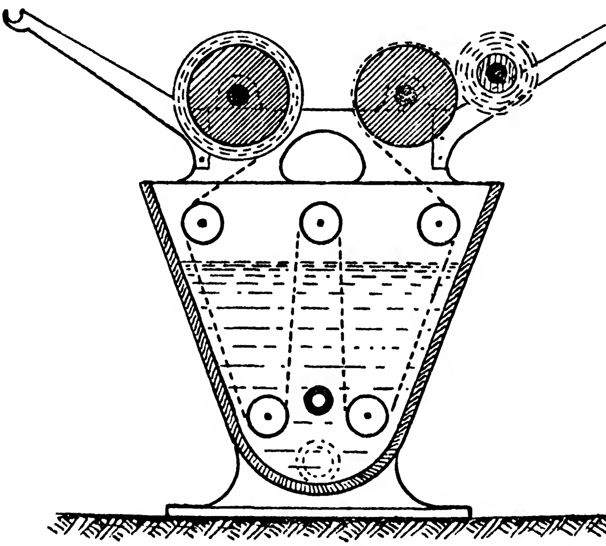


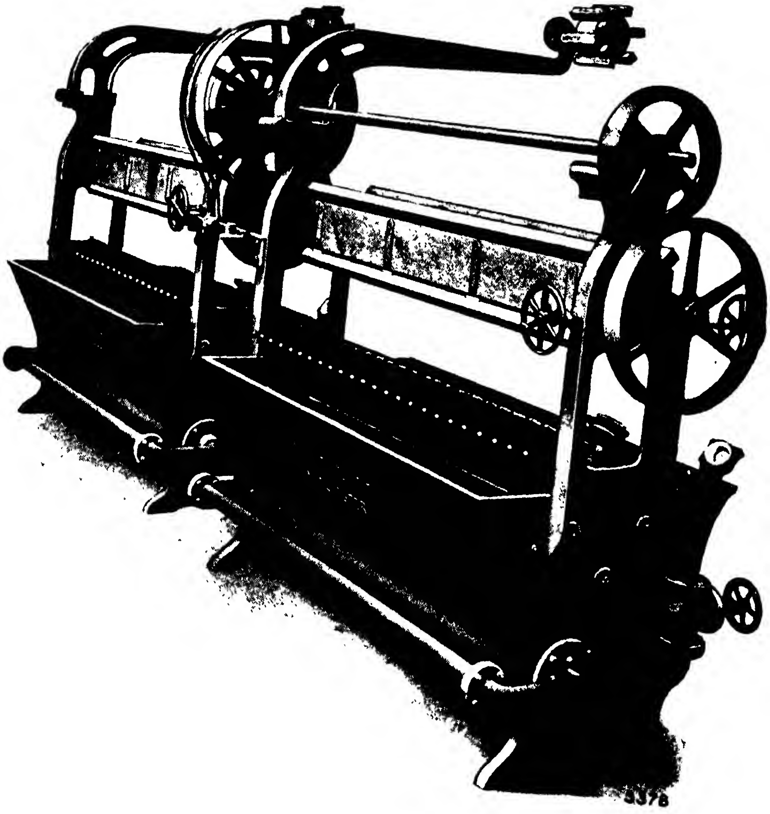
FIG. 65.—Jigger.

of continuous open dyeing machines is the same, to all intents and purposes, as that of fly dunging machines, except that the operations are carried out under different conditions of time and temperature. In both cases the goods are stitched end to end and run through the dye liquor in a continuous manner.

The *spiral dye beck* is the form of dyeing machine most largely used by calico printers. It is convenient, easy to work, gives regular results, and is capable of dealing with from 24 to 40 pieces of cloth at a time. In principle it is similar to the washing machine previously described (fig. 47), but differs from it in detail and general arrangement, a winch taking the place of the squeezer bowls, and the beck being rather different in shape.

Fig. 66 represents a cross-section of a spiral dyeing machine, from which an idea of its mode of action may be obtained. See also Plate IX.

AA is a long cast-iron dye beck fixed over the drain G; B is a midfeather or dividing board to keep the strands of cloth from becoming entangled; C is a perforated steam pipe for heating the dye liquor; D is a winch over which the cloth circulates continuously; E is a rail—the peg rail—carrying a series of pegs F, which serve as guides for the rope of cloth, and prevent the separate strands from running together and thus becoming entangled. The dotted circle round the winch represents the driving wheels, which may be actuated in any convenient way—either by cogs, straps, friction gearing, or an electric



Spiral Dye Becks.

[*To face p.* 176.

motor. Clutches, etc., are provided at the side of the machine for the purpose of knocking it in or out of gear as required.

The pieces of cloth to be dyed are first of all stitched end to end, so as to form a rope some 700 yards in length. One end of this rope is then introduced at one end of the machine, pulled over the winch and through the dye liquor, then over the winch again and through the dye liquor a second time, and so on until the beck is full. In this way the cloth passes over the winch and through the liquor in the form of twenty to twenty-five huge loops, each of

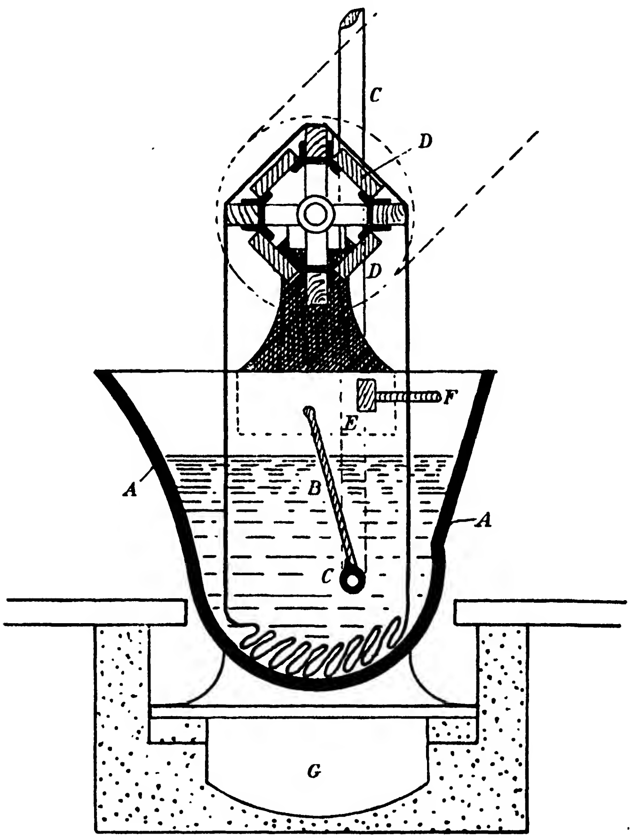


FIG. 66.—Spiral dye beck.

which is kept apart from those on each side of it by being made to run between the pegs F. When the first end of the long rope of cloth has traversed the full length of the dye beck it is brought back, horizontally and above the dye liquor, through two pot eyes and over two small pulleys, to the point at which it first entered the machine. Here it is sewn to the last end of the cloth, so that the whole forms an endless rope, passing through and through the machine in a spiral direction and in long slack loops. To guard against any possibility of the loops getting torn asunder by excessive tension, the lower part of each contains a few yards of slack cloth as shown in the diagram ; this "slack" falls down the inclined side of the beck in a regular manner, and, if the machine is in good order, it never increases in bulk from the beginning to the end of the dyeing.

Spiral dye becks can be used for a variety of operations, including washing, dunging, and soaping. When so used, it is almost needless to say that they ought not to be used for dyeing, each beck being reserved for the particular purpose for which it has been set aside.

(4) STEAMING.

Steaming consists in submitting the printed pieces to the action of steam for varying lengths of time and at different pressures.

In the early days of calico printing a very primitive, though to some extent effective, arrangement was used. The pieces were wrapped round a perforated steam pipe covered with printer's blanket to absorb the excess of moisture contained in the steam ; they were then enveloped in an outer covering of printer's blanket or other woollen material, and the steam, being turned on, penetrated through the whole cloth, thus effecting the decomposition of the various mordants, and their subsequent combination with the colouring matter with which they were mixed. This method of steaming is quite unsuited to many modern styles, and is now obsolete, except for the steaming of trial fents where no better system is available. Moreover, apart from the smallness of the output, the pieces were very unevenly steamed, and were subject to many objectionable defects, which need not be specified here, but which led ultimately to replacement by systems of steaming based on totally different principles.

Cottage Steaming.—The earliest of the improved methods of steaming consisted in hanging the goods in iron chambers into which steam was turned, and in which the goods could be treated under low pressure for any length of time. In a still more improved form this system is still used, and is known as "cottage" steaming, the name being derived from the fact that the early steamers were shaped like a cottage with gable ends, so as to allow of the condensed steam running down the inside of the roof instead of dropping on the suspended goods beneath. Fig. 67 shows a modern steaming cottage made by Messrs Mather & Platt.

It consists of a strong cylindrical chamber made of boiler plate, and provided with a door of dished steel plates which can be hermetically closed by means of stout bolts. Steam enters beneath a false bottom, so arranged that all chance of condensed water splashing on the pieces is avoided ; and the pressure is regulated by a safety-valve placed above. A cavity roof is also provided to which steam is admitted of a pressure higher than that admitted to the interior of the cottage, thus preventing condensation of steam and consequent drops of water on the cloth. The goods to be steamed are suspended from square wood rollers, the axles of which carry spur-wheels at one end, arranged to gear together when the iron carriage upon which the rollers are mounted is quite full of cloth. Through the side of the chamber extends a short shaft, the inside end of which carries a spur-wheel and the outside end a handle ; the spur-wheel gears into one of those on the square wooden rollers, and, when it is turned by the handle, transmits motion to every roller. In this way the position of the cloth on the rollers inside may be varied from time to time from the exterior in such a way as to ensure every part of the cloth being equally steamed. The carriage runs into and rests inside the chamber on rails laid down, above the false bottom, for its reception. Similar rails are laid down outside, and the two sets are connected, when the door is opened, by a couple of short lengths, so that the carriage can be run in and out with the greatest of ease.

In operation the goods are first of all wound between greys into large open

loops of full-width cloth; each loop, containing several pieces, is then placed on a separate roller, and when the carriage is full it is ready for entering. Meantime the cottage has been heated up by closing the door and allowing steam to pass through for some time: this is necessary in order to avoid as much as possible the formation of drops of condensed water, and generally to expedite the steaming. The carriage is then run in, the door closed, and steam turned on. For a short time it is allowed to pass right through the

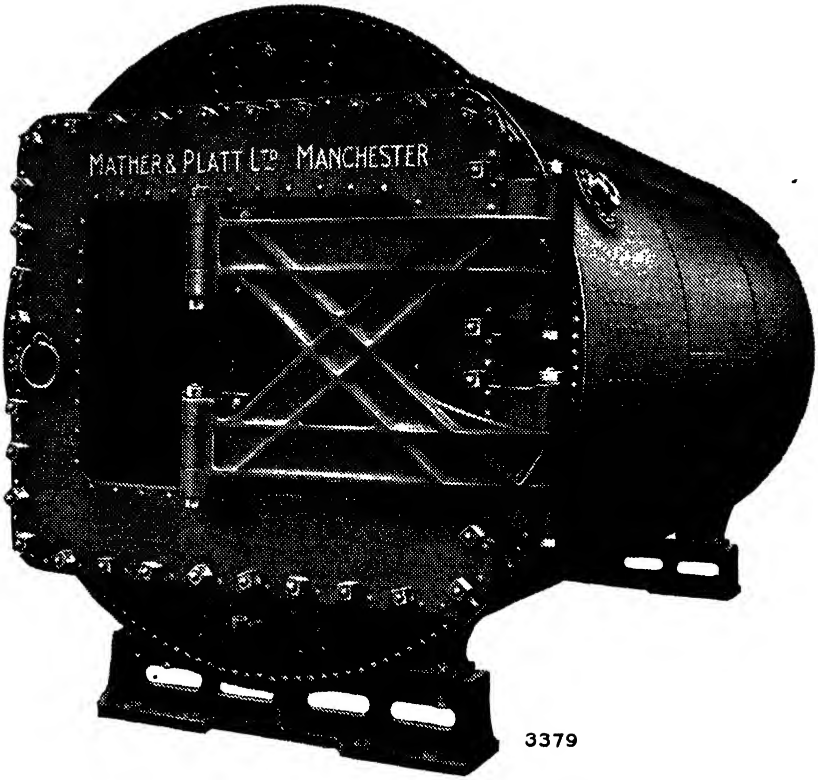


FIG. 67.—High-pressure steaming "cottage."

chamber, escaping by a pipe and valve below; finally the latter is closed and the steam pressure is allowed to rise to the desired extent, as indicated by a pressure-gauge, not shown. From time to time the condensed water (if any) is run from under the false bottom by opening the valve mentioned above. The steaming usually lasts from an hour to an hour and a half. The doors are then opened, the carriage drawn out, and the cloth removed from the rollers and unwound. The winding and unwinding are both done on the same machine—a revolving frame with four collapsible arms, something like an ordinary winch when the arms are extended.

In this apparatus steam pressure up to 30 lbs. may be used. Low-pressure steaming cottages are similar to the above, but less strongly built. They work up to 5 lbs. per sq. inch. High-pressure cottages are the more useful, since they can be worked at any pressure up to their highest limit.

Where small quantities of goods have to be steamed, the cottage is the most economical and convenient arrangement to use; and where goods have

to be treated by steaming under pressure, it is the only one available for the purpose.

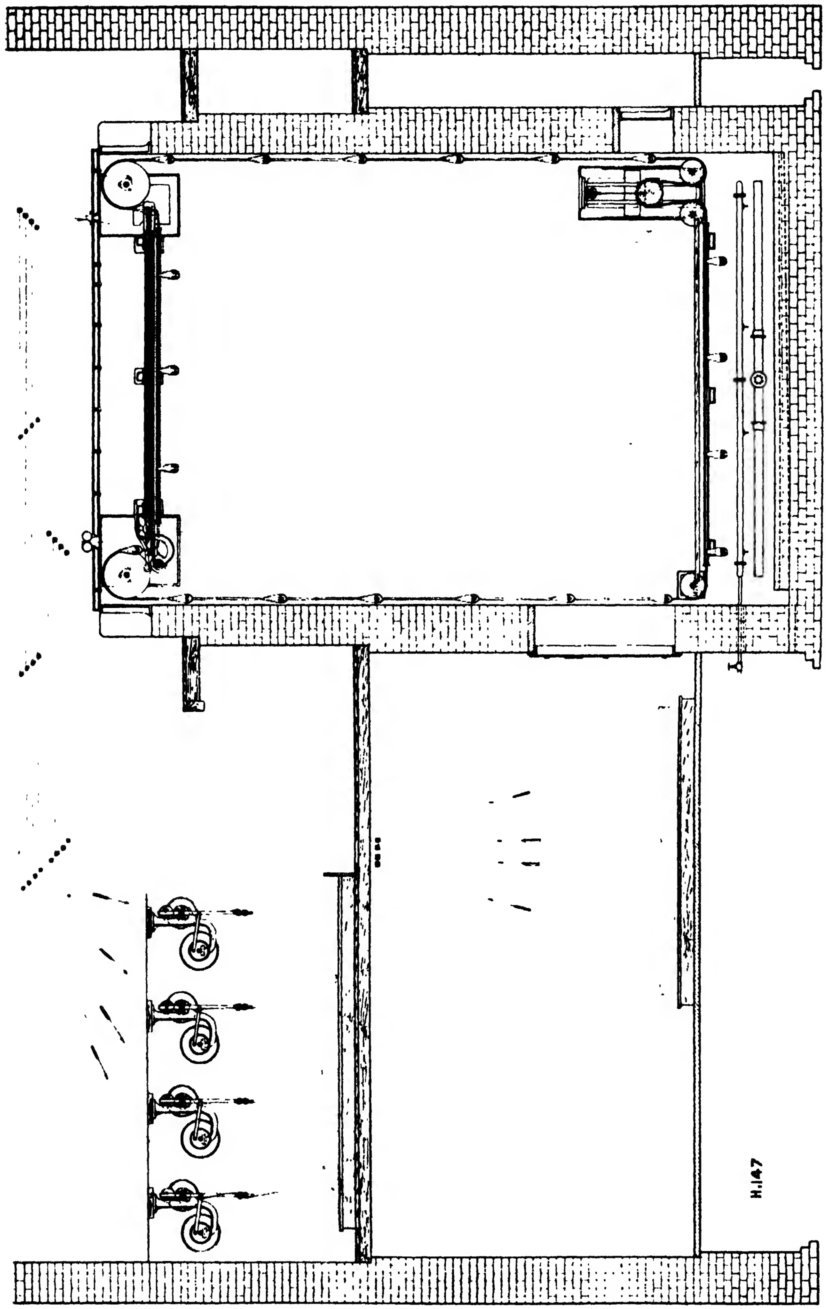
Continuous Steaming.—By far the most important system of steaming is that in which large quantities of goods travel slowly through an atmosphere of steam contained in a large closed chamber. The idea of this system, which is known as "continuous steaming," was originally conceived by Cordillot, but, as applied by him in practice, it had serious inherent defects, and it was not until Messrs Mather & Platt devoted their attention to the subject, and developed Cordillot's idea on totally new lines, that the system became a practical proposition. The first steaming apparatus with a brick chamber was erected in England in 1878. It was of a type now obsolete, and, though it marked a considerable advance on previous attempts at continuous steaming, it did not provide a complete solution of the problem. This solution came a few years later with the introduction of Mather's Continuous Steamer, which embodied the entirely new principle of passing the cloth continuously through the steaming chamber in the form of long loops suspended from brass rods or poles which were supported, and carried forward, by endless travelling chains. The introduction of this machine revolutionised the methods of steaming printed goods; and its principle of rod-carried cloth still forms the basis of the many types of continuous steamers manufactured by various makers in different parts of the world.

Since its inception the machine has undergone many alterations and improvements; notably in respect both of the means employed for operating the rods and of rendering it, at the same time, adaptable to a much wider range of styles.

Three types of continuous steamer are in current use, viz. (1) the original model with loose rods and separate carrying chains, (2) an improved automatic continuous steamer in which the rods are pushed forward along slotted races instead of being carried by chains, and (3) a new and greatly improved type of combined ageing and steaming machine in which the cloth is carried through the chamber suspended on rods which are permanently secured to specially designed chains.

The original model is no longer manufactured, but as many examples of it are still working satisfactorily in important works, and as it is of great historical interest, a description of its mode of action is not out of place here.

The apparatus consists of a large brick chamber (shown in Plate X.), roofed with steam-heated chests and provided at the bottom with a closed steam-heating coil which, in conjunction with the steam chests above, maintains the atmosphere of the chamber at a high temperature and prevents the condensation of steam. The necessary steam is admitted beneath this battery; and in order to avoid the pieces being splashed by any water that may enter along with it, the battery of heating pipes is usually covered with a wooden grating, over which pieces of old calico or of lapping are spread. At the top of the chamber two endless chains travel continuously from end to end of the apparatus. These chains run parallel with each other, one at each side of the chamber, and receive their motion from toothed driving wheels, over which they run. The centre part of each link of the two chains consists of a forked slot, into which rods drop automatically from time to time as the cloth runs into the chamber. The rods (of brass, covered with string or linen) are fed on to the chains at regular intervals by means of a corrugated drum, into the depressions of which they fit. This drum is arranged to deliver them on to a slide leading directly to the moving chains. In this slide they are held until a sufficiency of cloth has entered the chamber to form a long loop, somewhat less in height than the chamber itself; at this point one rod is released, slides



Automatic Continuous Steamer with Brick Chamber.

into the slots on the chains, and, in travelling forward with the latter, causes the cloth to fall over it, and thereby to begin to form itself into a second loop or fold. Simultaneously with this movement, the first rod carrying the upper loop of the first fold comes in contact with a swinging arm, or rather bar, which nips the cloth between itself and the rod, and thus prevents the weight of the first fold from dragging any more cloth over the first rod. If, for any reason, the swinging bar fails to act, the cloth, instead of hanging in folds, more or less equal in length, runs to the bottom of the chamber, and is dragged along in a tangled mass, with the result that it is unevenly steamed, and in ninety-nine cases out of a hundred is spoiled by absorbing moisture and picking up dirt from the coverings over the steam pipes. The first loop being properly suspended, the cloth continues to run into the machine until the second loop has attained its requisite length ; the second rod is then released, falls into position on the chain, and, like the first rod, causes the cloth to commence forming the third loop. At the same moment the first rod, in pushing the swinging bar forward, escapes from under it, leaving it free to swing backwards into contact with the second rod, with which it again nips the cloth exactly as in the first instance, and thus forces the cloth to run into the third loop. These operations are repeated uninterruptedly for every succeeding loop until the chamber is completely filled. The cloth is fed into the apparatus between two heated draw rollers of brass and falls perpendicularly, until its course is arrested by the entry of the various rods. On reaching the far end of the chamber, the goods are drawn out through a slit in the roof by means of plaiting-down tackle of the type shown on the left of Plate X. The rods leave the chamber at the same time, falling from the chains on to a drum similar to that by which they are introduced at the other end ; they are then transported by special travelling bands outside the chamber to the entering end again. In order to avoid the condensation of moisture on their surfaces, which might produce stains on the printed cloth, they are re-heated before they are allowed to enter the chamber again.

In the improved *Automatic Continuous Steamer* the travelling rod-carrying chains have been discarded in favour of slotted guides, fixed one on each side of the chamber—an arrangement much less liable to get out of order than chains. Into these slots or races flanged brass rods are inserted automatically, and are pushed forward by a pair of cams at such speed as to ensure that the cloth is fully steamed. At the exit end of the machine the cloth is drawn out as above, and the rods are automatically picked up by hooks on a pair of endless chains and carried round the chamber to the entering end again, without requiring to be otherwise handled in any way. The advantages of this improved system are that (1) the rods are always at the same temperature ; (2) that they are not exposed to the risk of damage, inseparable from constant handling ; and (3) the rods cannot well get out of alignment, or fall into the bottom of the chamber, as frequently happens in the older type of continuous steamer when the carrying chains become worn. The automatic cam movement is extremely simple and durable ; and as its installation involves no structural alteration of the steaming chamber, it can be applied without difficulty to existing machines that are at present working on the old chain principle.

Plate XI. shows a section of this improved automatic continuous steamer, in which four pieces are being steamed together.

The Continuous Automatic Steaming and Ageing Machine.—This machine represents the third and most perfect type of steamer in current use. As its name implies, it combines the essential features of both the Continuous Steamer and the Rapid Steam Ager. It is built entirely of metal, and in this connection

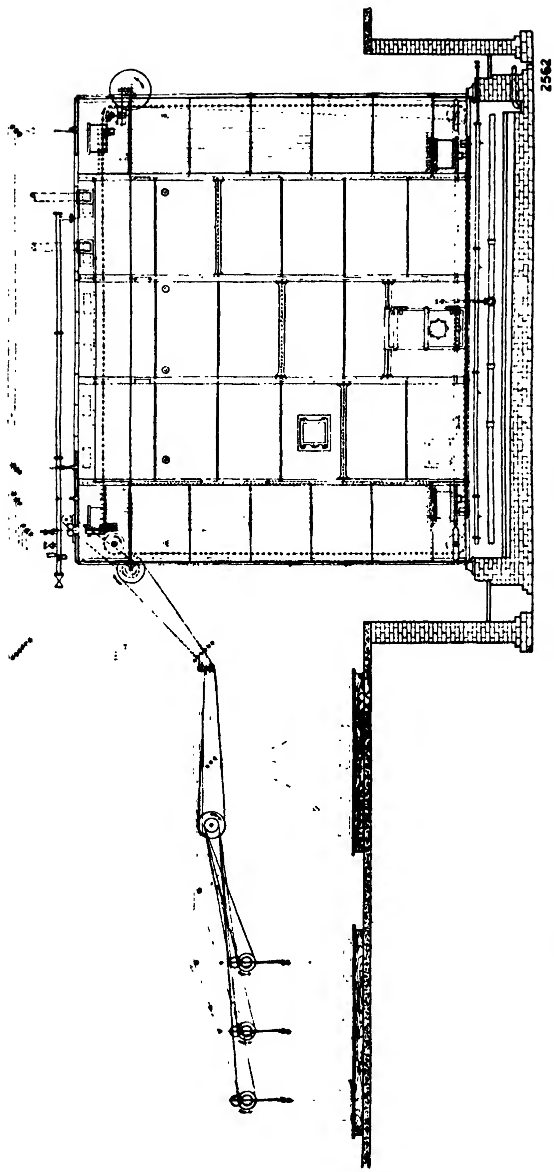
it is interesting to note that Messrs Mather & Platt, Ltd. were the pioneers in the construction of all-metal steamers, having introduced a small continuous steamer of this description in 1894.

As will be seen from the longitudinal section of the machine shown in Plate XII., the principle underlying the construction is the same as that which had been employed successfully in the design of previous types. A new feature has been introduced in the form of " pole chains "—a combination of the cloth-carrying poles or rods with two Renold's *roller* chains, which replaces the separate poles and chains used previously for transporting the cloth through the steaming chamber. This improvement has been rendered possible only by the recent introduction of *roller* chains of a design and material capable of withstanding the exacting requirements of this class of machine and of working satisfactorily, for long periods, under conditions of heat and humidity previously considered unsuitable for any type of *roller* chain.

The walls of the chamber are built of steel plates and strong rolled-steel sections securely bolted together to form a rigid structure ; ample provision is made, in the way of doors and plate-glass windows, for access to and inspection of the interior ; and the whole is covered in by a roof of cast-iron steam chests. The chests are constructed for a working steam pressure of 5 lbs. per square inch, and they not only contribute to the heating of the chamber but also facilitate, without risk of condensation, the use of the almost saturated steam which is necessary for the proper fixation of vat colours.

An advantage possessed by the all-metal chamber over the brick chamber of earlier steamers is that the defects and troubles, such as cracking, sinking of foundations and the necessary pointing, etc., which are inherent in brick structures, are entirely obviated. Moreover, the recessed spaces in the sides and ends of the chamber, arising out of the method of its construction, afford excellent hold to the non-conducting material with which the machine is insulated and, by maintaining the insulation in an uncracked and efficient condition, enable the requisite temperature to be reached rapidly and retained easily.

The Automatic Steaming and Ageing Machine is designed to deal with practically every style of printing which requires an exposure to steam to develop the colours. It provides for a very wide range of steaming periods and, by careful selection, it is possible to steam three different styles for three different periods concurrently. As shown in Plate XII., apertures or exits are arranged at various positions in the roof to permit of the withdrawal of one or more pieces of cloth after the appropriate period of steaming has elapsed. Thus, it is possible to run into the chamber simultaneously three such dissimilar styles as Vat colour prints, hydrosulphite discharge work, and ordinary steam styles containing Basic, Alizarin, vegetable, and Chrome mordant colours, and to withdraw each style separately, from different apertures along the roof, as soon as it has received its appropriate steaming. This mode of treating different styles together for widely different periods is, of course, economical only when the proportion between the quantity of goods requiring a long steaming and the quantity of those requiring only a short steaming is such that the whole capacity of the steaming chamber is fully utilised during the whole period required for the longer process. It would be manifestly absurd to heat and fill the chamber with steam if, for most of the time, only a quarter or less of its length were required for short-steaming or ageing purposes. In such cases as, for instance, where there is a large production of such styles as Aniline blacks, Vat colour prints, hydrosulphite discharges or resists under mordants, and only a relatively small production of long-steam styles, it is obviously more



Automatic Continuous Steamer with All-metal Chamber (Mather & Platt, Ltd.).

advantageous to make use of the smaller Hydrosulphite-Aniline Ager (fig. 60) for steaming the bulk of the work. On the other hand, when *long-steam* styles predominate, the employment of the new and improved Continuous Automatic Steaming and Ageing Machine is clearly indicated as being the most expeditious, economical, and efficient means of dealing with the production as a whole.

The *modus operandi* of the All-metal Continuous Automatic Steaming and Ageing Machine is generally similar to that described for the older brick chamber continuous steamers; the poles or rods, however, are not loose but form part of the chains which carry them round the chamber. The ends of the poles are secured permanently to the opposite links of two parallel travelling Renold's roller chains—a method of construction which dispenses entirely with the rather complicated mechanism previously required to return the poles to the entering end of the chamber. In appearance these so-called "pole-chains" resemble a flexible metal ladder with wide, close-set, brass rungs.

The number of printed pieces and greys passed into the chamber at one time may be varied to suit requirements and, as usual, their entry is regulated by a pair of steam-heated draw rollers arranged immediately over, and in close proximity to, the first aperture in the roof of the chamber. On leaving the draw-rollers the cloth passes through a "manger" (which serves the double purpose of ensuring its vertical fall and of guiding it directly on to the poles) and automatically falls into long loops or laps on the poles which, as already mentioned, constitute an integral part of, and connect together, the two travelling roller chains. As the chains move slowly forward, each pole, in turn, is brought up against the constantly falling cloth and gradually pushes it forward until it drops *over* the pole in question and begins to form a fresh loop between that and the next advancing pole. Thus the process goes on automatically for as long as required. The cloth-loaded pole-chains slide in machined races at each side of the chamber. These races or rails, in addition to acting as guides, also preserve the horizontality of the chains at the top of the chamber, prevent them from sagging under their load, and by taking the whole weight of the cloth-loaded portions of the pole-chains relieve the end links of those portions from the enormous strain that, otherwise, would be imposed upon them. The sprocket wheels, over which the chains run, being driven by worm gearing from the main cross-shaft of the machine, impart a smooth and steady motion to the pole-chains, and, as a result of this even drive, the cloth is automatically conveyed through the chamber for the required distance and time, without fear of the long loops (or laps) becoming disarranged or falling into the bottom. As already noted, it is possible to steam two or three different styles at the same time for different periods and to withdraw each, independently, through different exits arranged at various positions in the roof of the chamber, after the requisite period of steaming is completed. The pieces are withdrawn by plaiters, three of which are shown at work in Plate XII.; in this case only one style is being dealt with, but the apertures for the withdrawal of short-steam styles are also shown in the plate, and the method of dealing with them is the same. The plaiters may be regulated in speed to avoid any undue tension on the cloth. In order that the whole body of the cloth may receive equal treatment, a very simple and effective device is provided whereby each pole may be rotated at intervals during the passage of the cloth through the chamber, thus exposing every part of it to the full action of the steam.

The necessary atmosphere and temperature in the chamber are obtained from closed heating coils and perforated steam pipes situated in the bottom of the chamber under a wooden lagged floor.

The results which have been obtained on the machine just described have more than realised the highest expectations, and users have testified to the following outstanding advantages:—(1) A marked advance on any known steamer; (2) the power required to drive and the upkeep charges are reduced to a minimum; (3) perfect results; (4) advantage over ordinary agers in that the *printed side* of the cloth does not come into contact with heated metal rollers (or poles) and consequently no "marking off" occurs; and (5) aged and steam styles may be treated together at the same time.

Other continuous steaming machines are in use both in England and on the Continent—notably, that manufactured by John Wood, which may also be employed as an ageing machine, and the Remy-Welter steamer (*Société Alsacienne pour Constructions Mecaniques*), which is adapted only for long steaming. Neither of these machines calls for detailed description, as both conform fairly closely with one or other of types already described.

Notes on Steaming.—With proper care, and handled with experience, all continuous steamers by reputable makers yield excellent results notwithstanding the fact that the folds of cloth frequently rub against each other before the colours printed upon them are fixed. All the same, accidents are liable to occur if certain precautions are neglected. In the first place, the chamber must be heated up thoroughly before any cloth is entered; and in the type of machine where the rods are taken out when they reach the back end of the chamber, they must be heated in order to prevent moisture from condensing upon them when they re-enter the chamber. Moisture, from any source whatever, condensing on the pieces, causes the colour to run. All parts of the apparatus, therefore, should be perfectly dry and hot before any work is commenced, otherwise mishaps are almost sure to happen. The cloth itself, too, ought to be warm and dry previous to entering the chamber. These conditions are usually fulfilled by storing the goods in a warm room contiguous to the steamer, and, further, by passing them into the steaming chamber between the heated brass rollers already mentioned. Apart from condensation on the rods and fittings of the machine, it frequently happens that drops of water fall on the pieces from holes in the steam chests which form the roof of the chamber; if the hole is comparatively large, the drops produce large spots; but if it is very minute, the condensed water is forced out as fine spray by the pressure of steam behind it, and causes the colour to run into irregularly shaped patches, extending over a considerable space. These various faults are easily distinguished from each other; their shape and general appearance afford a clue to their origin. If the colour has run from side to side of the piece in a straight line, the defect may safely be attributed to a damp rod; if drops appear irregularly distributed over the piece, general condensation is taking place on the roof of the chamber; if, however, the drop-marks always occupy the same relative position, they will, as a rule, be found to proceed from a perforation in the roofing steam chests, and the same may be said of the effect of spray, the only differences between the two faults being (1) in the extent of the space over which the colours run, and (2) that drops produce spots with light centres, whereas a spray gives a more or less cloudy patch. Another fault to guard against is the marking off of the colour from one fold of cloth to another. Many colours contain an appreciable quantity of oil and fatty matters, and these are very apt to mark off on anything with which they happen to come into contact. Again, soluble or hygroscopic bodies which absorb a large amount of moisture in steaming, and oxalic and other acids which exercise a decomposing action on starch, etc., are all exceedingly liable to mark off during the steaming operation, unless the laps of the cloth upon which they are printed are prevented from rubbing against each other in the steamer.

In practice, therefore, all such goods are steamed along with a piece of grey cloth, so arranged that the printed sides of the goods (hanging in loops) are separated from each other by two folds of the grey cloth, which receives any colour that would otherwise be transferred to the printed pieces themselves. Very heavy patterns penetrating through to the back of the cloth and reversible prints are steamed between two greys if their colours are in any way likely to mark off; and when two pieces are steamed together they are run, printed face to printed face, with a grey cloth between them. In this way all danger of marking off is avoided. When very light patterns are steamed, four pieces may be run together, without any special precautions, provided the colours on each piece do not contain anything detrimental to each other.

A further important point to be taken into account is the condition in which the goods are sent up for steaming. If they pass directly from the printing machine to the steamer, the colours, being hard and dry, require a much moister steam for their development than if they had been allowed to lie for an hour or two to cool down. During the cooling they absorb a certain amount of moisture from the atmosphere, and then if they are exposed to the action of steam that is too moist they absorb a still further amount, becoming so damp that the colours run at the edges of the design and tend to mark off whenever two laps come in contact with each other. Some printers pass such styles as Vat colour prints through the Sjöström Cooling and Conditioning Machine immediately after they leave the drying chamber of the printing machine, in order to impart to them the necessary moisture.

It is obvious, therefore, that the working of a steaming apparatus requires experience and no little attention if the best results are to be secured. No matter how perfect the machine may be mechanically, no good work can be executed by it unless the foregoing simple precautions be observed to the letter, and due regard be paid both to the state in which the cloth is presented to the action of the steam and to the humidity of the steam itself.

(5) FIXING.

The term *fixing* in its widest sense may properly be applied to all operations connected with the precipitation of mordants and colouring matters on the fibre; and in this sense it would include ageing, dunging, steaming, etc. As generally understood in printworks, however, fixing consists in passing printed or mordanted goods (other than Madder styles) through solutions of various salts, etc., which either precipitate the mordant in the form of an oxide, hydroxide, or insoluble salt, or increase the complexity and insolubility of an already formed colour-lake. For example, the lakes produced by the combination of tannic acid with Basic aniline colours are too soluble to withstand soaping, but if they be treated with a solution of tartar emetic they are converted into insolüble double or compound lakes, consisting of the tannates of antimony and of the colour-base; and as these compound lakes are insoluble in water and soap solutions, the colouring matter is said to have been fixed by the tartar emetic. In the case of goods prepared in, say, chromate of chromium, the mordant is fixed upon the fibre as an insoluble hydroxide by passing the pieces through a boiling solution of sodium carbonate. In this way, by using suitable fixing agents, many colours and a few mordants are easily capable of being attached to the fibre in such a manner as to resist washing in water, alkaline solutions, or soap; in a word, they are fixed, and become either fast colours or the bases upon which fast colours are dyed.

The methods of effecting this fixation vary considerably. Cloth printed in Basic colours is passed in the open width, after steaming, through a solution of

tartar emetic or other antimony salt, contained in a small box or beck attached to, and forming part of, the open soaping and washing machine; chromium and lead salts are precipitated either in jiggers or becks provided with top and bottom rollers over which the cloth passes continuously—and sometimes in the open soaper, the first compartment of which is filled with sodium carbonate, sodium sulphate, milk of lime, etc., as the case may require; and basic lead mordants, padded on the cloth, are fixed in a chamber filled with ammonia vapour. But no definite instructions can be given for any and every method of fixing, as the machinery used for the purpose differs in different works; as a rule, any plant will do if the cloth can be passed through it in the open width under the requisite conditions of temperature, and without entailing any waste of material.

Most of the fixing agents in general use have been given when treating of the dunging process, so that it only remains here to mention the antimony salts.

Tartar Emetic or Antimonyl Potassium Tartrate [$K(SbO)C_4H_4O_6 + \frac{1}{2}H_2O$] is the best known of these salts. It is only sparingly soluble in water, but is nevertheless the most largely used of all fixing agents of its class, and as a precipitant for tannic acid it gives excellent results, especially in the presence of chalk, common salt, and other neutral salts. It is worthy of note that tartar emetic dissolves much more readily in a solution of common salt than in water. Tartar emetic contains 43 per cent. Sb_2O_3.

In using tartar emetic as a fixative for tannic acid, it is important to remember that the bath gradually becomes acid through the formation of acid potassium tartrate by the abstraction of antimony. If allowed to accumulate, this salt dissolves the tannate of antimony or colour-lake, as the case may be, and thus not only prevents its fixation on the fibre, but actually strips or dissolves it from the cloth. A little chalk added to the bath neutralises the acidity, and allows of the goods being run through continuously.

Double Oxalate of Antimony and Potassium [$K_3Sb(C_2O_4)_3.4H_2O$] is an efficient and cheap substitute for tartar emetic. It only contains 25 per cent. Sb_2O_3; and although it is weaker in antimony, it yet produces the same result, weight for weight. This is due to the fact that it dissociates more easily, and thus gives up its antimony more readily than tartar emetic. Another advantage is that it can be used longer than an equally strong bath of tartar emetic without injuring the goods.

Sodium Tartar Emetic [$Na(SbO)C_4H_4O_6.\frac{1}{2}H_2O$] is much more soluble than the potassium salt, but it is not much used as a fixing agent, its chief employment being for the production of reserve effects under basic colours.

"Antimony Salt" [$SbF_3 . (NH_4)_2SO_4$] contains about 47 per cent. Sb_2O_3, is fairly soluble, and can be used in place of tartar emetic for all purposes. About nine parts of antimony salt equal ten parts of tartar emetic.

Antimony Sodium Fluoride ($SbF_3.NaF$) contains an amount of antimony equal to about 66 per cent. Sb_2O_3, and is therefore half as strong again as tartar emetic; it is very soluble, and can be used for most of the purposes for which tartar emetic is used.

Lactate of Antimony, or Antimonin, comes into the market as a moist yellow mass, or in soft lumps, with the unpleasant smell of decayed cheese. It contains about 15 per cent. Sb_2O_3, the whole of which is available; consequently, as a fixing agent it is equal to the same weight of tartar emetic. In practice it is dissolved in water with the addition of a little acetic acid, otherwise it gives a turbid solution.

Freshly prepared *antimony hydrate* is stated by Hummel to be an economical fixing agent for tannic acid, and to possess the advantage of not leaving the bath acid. It is doubtful whether it is used in practice for this purpose.

Details respecting the preparation of fixing liquors will be found in Part VII. (Styles of Printing), where they will be given along with the processes of which they form a part.

(6) RAISING AND DEVELOPING.

Raising or developing only differs from fixing in that the colours are not merely fixed on the fibre, but are actually produced thereon at the same time. Amongst the colours so produced, the most important are the mineral pigments, Chrome yellow, Iron buff, Prussian blue, and Manganese brown. Salts of lead, iron, and manganese are printed on or otherwise applied to the cloth, and the colours are raised from them by simply passing them through the following solutions: bichromate of potash for Chromate of lead yellow; caustic soda for Iron buff; a ferrous or ferric salt for Prussian blue; and caustic soda and bleaching powder for Manganese bronze.

The development of Catechu brown and other vegetable dyestuffs, and also of Aniline black, by running through a hot solution of bichromate of potash, may also be looked upon as a species of raising, though, strictly speaking, in the case of the vegetable colours it is a true mordanting process, and in that of Aniline black an oxidation process. At the same time it is performed exactly like fixing and raising, and in a similar apparatus, and might therefore be classed with either of those operations.

The development of the Azoic colours is a subject apart, and will be considered separately; and other information concerning raising will be given, under the heading of Raised Styles, in a future section.

(7) CUTTING.

Cutting is a technical term used to denote the effect produced by discharging agents on dyed colours. If the dyed ground is discharged perfectly, it is well cut; if only partially, it is badly cut. In this sense cutting is a general term, but when applied specifically it is usually understood to refer to a particular stage in the production of coloured patterns discharged on Indigo-dyed cloth by the chromic acid method. The cloth is printed with a paste containing chromate of soda, dried, and passed through a warm solution of sulphuric and oxalic acids—the cutting bath—when chromic acid is liberated and oxidises, and so destroys the colour of, the Indigo wherever the chromate was originally printed.

Caustic soda may also be classed as a cutting agent for Indigo-dyed goods when the latter are printed by the Rongalite-Leucotrope process or with ferricyanide of potash, according to O'Neill's process of Indigo discharging. Oxymuriate of tin was also called a cutting liquor in the days when Madder or Swiss pinks formed an important article of manufacture.

Neither of these two latter styles are at present in vogue—nor ever again likely to be; and in consequence cutting may be considered (when used to designate a distinct process) as an essential operation connected with one particular class of work, namely, Indigo discharge.

(8) WASHING.

The thorough washing of the cloth, after almost every operation through which it goes in the course of being transformed into a *printed* fabric, constitutes one of the most important branches of calico printing.

Formerly the output of printed goods was so small, and the streams upon which printworks were situated so clear, that the necessary washing of the goods was done by simply allowing them to float in the stream, or in specially constructed stone or wooden troughs and channels, through which the stream was caused to run. For the class of work then produced, this primitive system was perhaps efficient; but as the industry advanced and new processes were introduced, a more rapid and more thorough method of washing was required, in order to cope both with the increased demand for printed goods and with the necessity for removing as perfectly as possible the thickening materials used in printing.

One of the oldest washing machines devised for this purpose, and still used

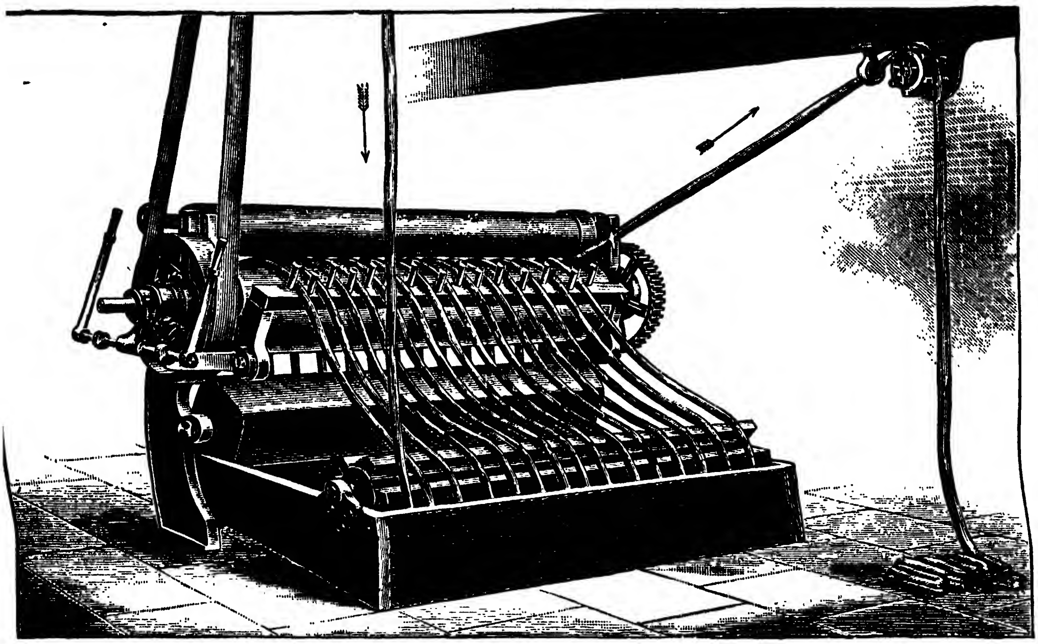


FIG. 68.—Square beater washing machine.

to some extent when existing, is the "dash wheel." It consists of a large revolving wooden drum, mounted on bearings, fixed on each side of a drain, in which the wheel works. It is divided inside into four or more compartments, separated from each other by wooden gratings, and each compartment has a round opening in the side for the introduction of the goods. Jets of warm or cold water are arranged to play on the cloth through slits in the sides and circumference of the wheel and the dirty water escapes through the same slits and holes into the drain beneath. Each compartment is large enough to hold 3–4 pieces of cloth loosely bundled up, and during the revolution of the wheel they are dashed from side to side, and from centre to circumference. The process is slow, but the washing is good, and the thickenings get loosened and removed by the constant tossing about of the cloth.

Figs. 68 and 69 represent the elevation and section of one of the most useful, most inexpensive, most largely used, and simplest washing machines. It consists of a long and wide shallow trough, provided with a square beater and lagged winch. Immediately above the beater is a pair of squeezing bowls of pine. In the machine here shown the cloth is only squeezed as it leaves the

machine, the end of the upper bowl being furnished with a white metal ring, between which and the lower bowl the cloth is nipped. The pieces travel spirally through the machine between the rollers ; and the action of the square beater, which revolves in a direction contrary to that of the pieces, is to open out the cloth from the rope state to almost its full width as it passes along the surface of the water, so that every part of it receives a flapping motion which effectually beats out loose particles of thickening, mordant, or dyestuff, etc.

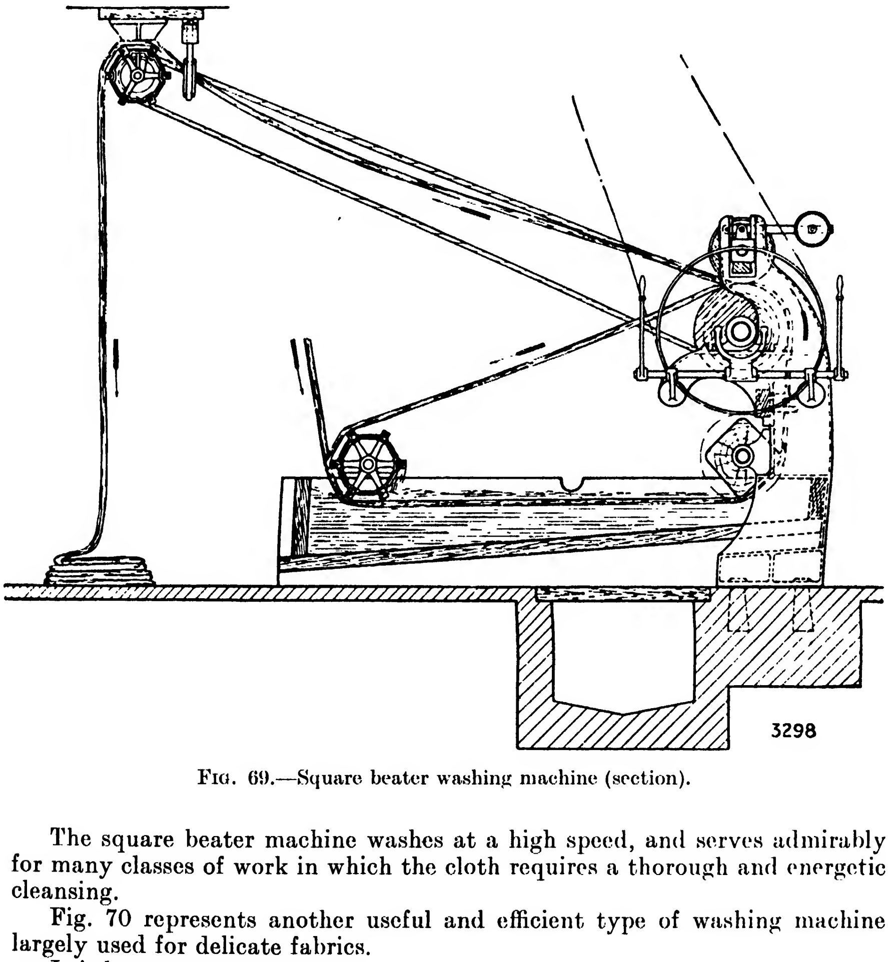


FIG. 69.—Square beater washing machine (section).

The square beater machine washes at a high speed, and serves admirably for many classes of work in which the cloth requires a thorough and energetic cleansing.

Fig. 70 represents another useful and efficient type of washing machine largely used for delicate fabrics.

It is known as the " slack washing machine," and can be used in either the dye-house or the bleach-house in all cases where it is important to avoid putting any tension on the cloth. The goods pass through, as usual, in a continuous manner, and spirally, and receive a very efficient wash from the water expressed by the squeezing bowls.

A new type of slack washing machine, recently introduced, has been designed specially to comply with the conditions required in the washing of the most delicate fabrics, such as Georgette, Crêpe de Chine, Charmeuse, Rayon and its mixtures with cotton, and various other silk and artificial silk materials, to which it is undesirable to apply any sort of tension or pressure.

The machine, which is adapted as well to scouring as to washing, consists

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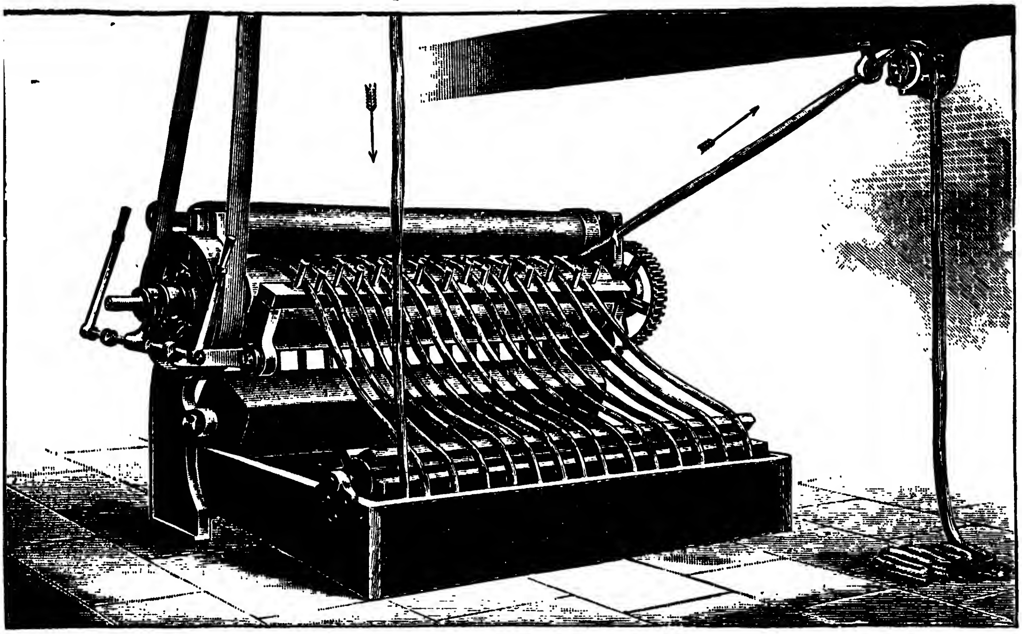

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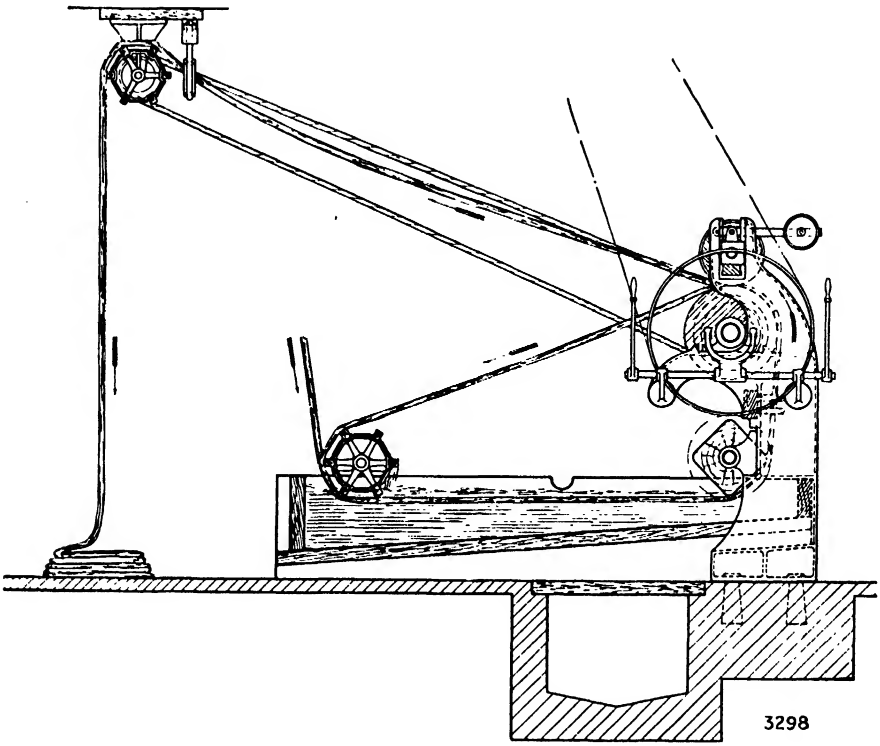

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The machine, which is adapted as well to scouring as to washing, consists

essentially of a large elliptical wince fitted at one side of, and above, a long, wide, and shallow beck or trough, a peg rail, and a small circular wince fitted at the other side of the beck for drawing the cloth through the wash water and delivering it to the peg rail. In operation, several pieces of cloth (varying in number according to the width of the machine), each having a length of from 60 to 120 yards, are threaded separately between the pegs and over the two winces; the ends of each piece are then sewn together, thus forming a series of endless loops in which a considerable amount of slack is allowed in order to give ample time for the wash water (or scouring liquor) to penetrate

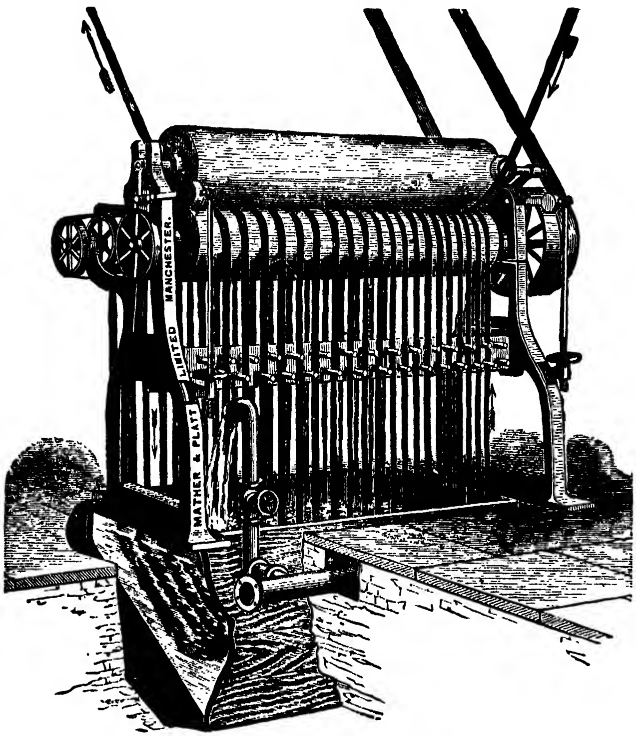


FIG. 70.- Slack washing machine.

into the cloth. The penetration is materially assisted by the elliptical wince, which gently flaps the wet cloth as it draws it over the peg rail and, by plaiting it down in the beck with a to-and-fro motion, causes it to swish gently as it enters the water. The pieces are kept apart by the peg rail, and any tendency of the strands to float and to become entangled is obviated by a wooden partition or midfeather extending to just below the surface of the water; a further precaution against entanglement is provided in the front part of the beck where, by the insertion of a perforated wood partition, a separate compartment is formed into which additional water or scouring liquor may be introduced as required. This compartment is furnished with silent injector heating nozzles to reduce the ebullition of the liquor to a minimum when boiling, and thus, in scouring operations or hot-water washes, the steady circulation of the separate loops of cloth is undisturbed by the turbulence of boiling liquor.

On completion of the washing (or scouring), the machine is stopped and the ends of the pieces of fabric are unsewn and placed on the delivery side of the

elliptical wince in such a way that one end of each piece is suspended on the wince while the other end remains in the beck. A perforated draining board is now slipped under the wince which, when the machine is started again, withdraws the pieces from the beck and plaits them on the board, the excess of water draining back into the beck. After draining thoroughly, the pieces are plaited over a delivery wince into waggons in readiness for hydro-extraction or other process (see fig. 71).

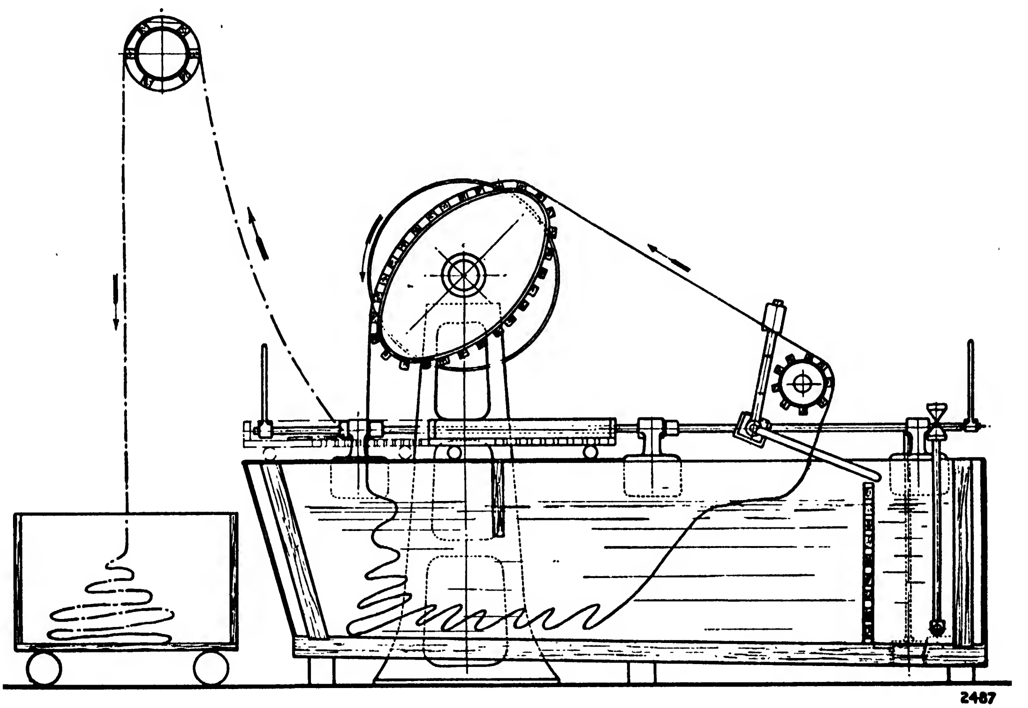


FIG. 71.—Elliptical wince washing machine.

No squeezing bowls are used at any stage. The pieces are treated throughout without either pressure or undue tension, and emerge from the process undistorted and undamaged.

The machine is usually driven by a pair of fast and loose pulleys from a line shaft. If, from any cause, the strands of cloth become entangled in process, the machine is instantly stopped by an automatic knock-off motion placed between the peg rail and the driving pulleys.

The washing machine shown in fig. 47 is also largely used for all purposes of cleansing printed goods in all stages of manufacture. Two pieces of cloth may be washed at the same time if desired, and when this is possible the production of the machine at full speed is 400 yards per minute. The same type of machine is employed for souring and chemicking in the bleach-house, and if fitted with heating arrangements may be used for a variety of other purposes —raising, etc.—apart from washing.

Excess of water is usually removed from the washed calico by passing it between a pair of squeezing bowls. A machine suitable for this purpose is shown in fig. 72.

As will be seen, it consists of a wooden trough and a pair of sycamore, coco-fibre, or compressed cotton bowls, mounted in a strong framework. The pressure of the top bowl on the bottom one is adjusted by powerful compound weighted levers. The cloth, after undergoing a final rinsing in the water trough, passes through two pot eyes, between the pressure bowls, and emerges on the other side free from all surplus water, and in a fit state for opening out and drying over steam-heated cylinders. In this machine two strands of cloth are treated at the same time, and the unequal wearing of the bowls is provided against by giving the pot eyes through which the cloth passes a traversing

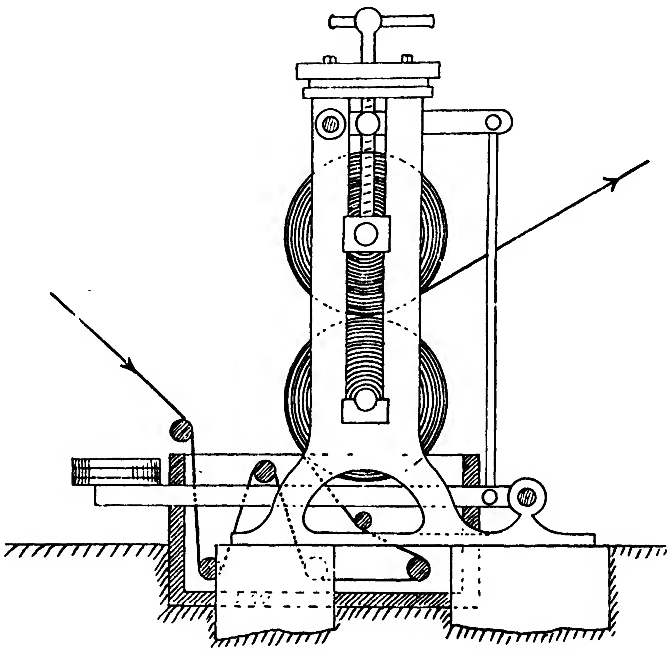


FIG. 72.—Dye-house squeezer.

motion, whereby the cloth is made to travel from side to side continually during the whole time that it is passing between the bowls.[1]

In Birch's squeezer the plain pressure bowls are replaced by grooved rollers. The cloth is compressed in the narrow grooves of one roller and squeezed by the projecting corrugations of the other, which fit into the grooves of the first.

Squeezing machines are for the most part confined to bleach-house work; printed and dyed colours would mark-off on the white ground and on each other if passed in the rope state between pressure bowls.

(9) SOAPING.

Soaping is another important operation connected with the final cleansing of dyed and printed goods.

Its object is twofold: (1) to clear the white unprinted ground of the cloth; and (2) to brighten the colours by removing all extraneous matters and the by-products resulting from the lake-forming reactions. These objects are attained

[1] The travelling pot eyes have been omitted inadvertently in fig. 72. They occupy a position in front of the upper bowl.

by means of two different types of machine: the *Open Soaping Machine* and the *Spiral Soaping Machine.*

The advantages of soaping printed goods in the full open width are too obvious to mention; in fact, they are so generally recognised that an open soaper of some sort is to be found in every printworks.

(1) The machine illustrated in fig. 73 consists of separate cisterns, and may be used for a variety of purposes, including raising, fixing, cutting, chroming, developing naphthol colours, and, of course, the washing and soaping of these styles. In fig. 73 the machine shown consists of six cisterns only, but any number may be added if required. Each cistern is fitted with brass top and bottom guide rollers, and at suitable intervals heavy squeezing bowls of brass and rubber, or brass and sycamore, are provided to express the excess of dirty water, soap liquor, or other solutions. With the exception of the first cistern, all the cisterns are fitted with patent non-corrodible metal beaters, placed partly immersed in the liquor and between each lap of cloth; they are driven, independently of the guide rollers, at a high speed, and being extremely simple in construction, are very durable and not liable to get out of order. The effect of these beaters is to dash the liquor with great force upon both sides of the travelling cloth, and thus thoroughly cleanse it by loosening and removing all thickening agents and any fixing or raising liquors that may have been used in the first cistern—and this without injuring in the slightest degree the most delicate

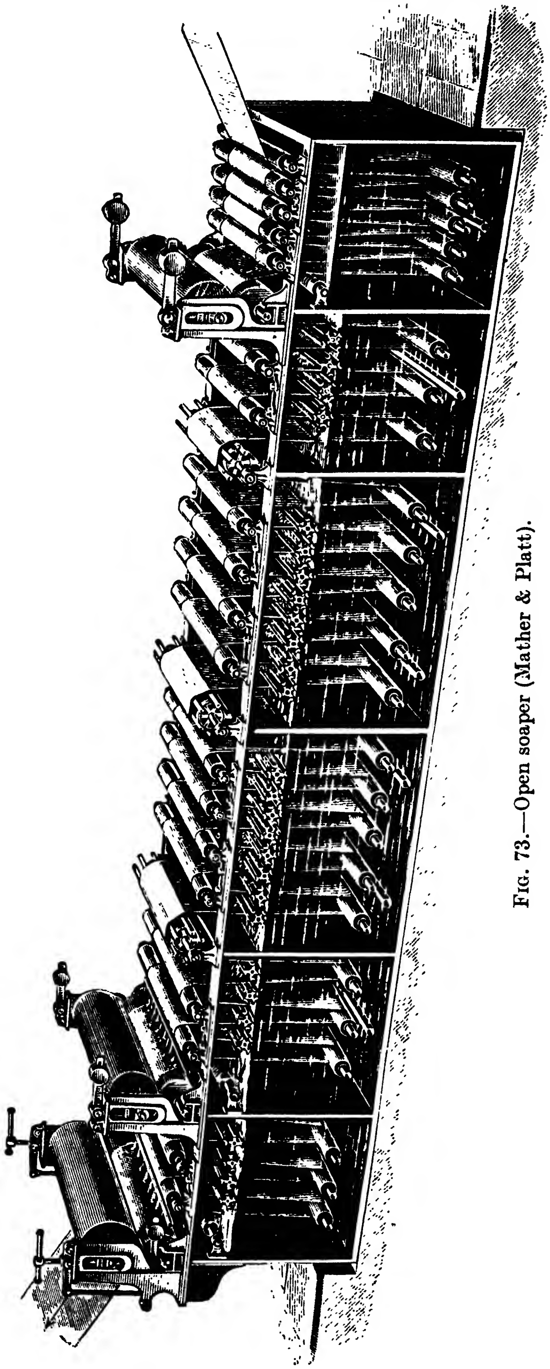


Fig. 73.—Open soaper (Mather & Platt).

fabric. The jets of water from the spirt pipes (fixed in front of the two last pairs of bowls) further aid in removing the last traces of soap, etc., from the cloth.

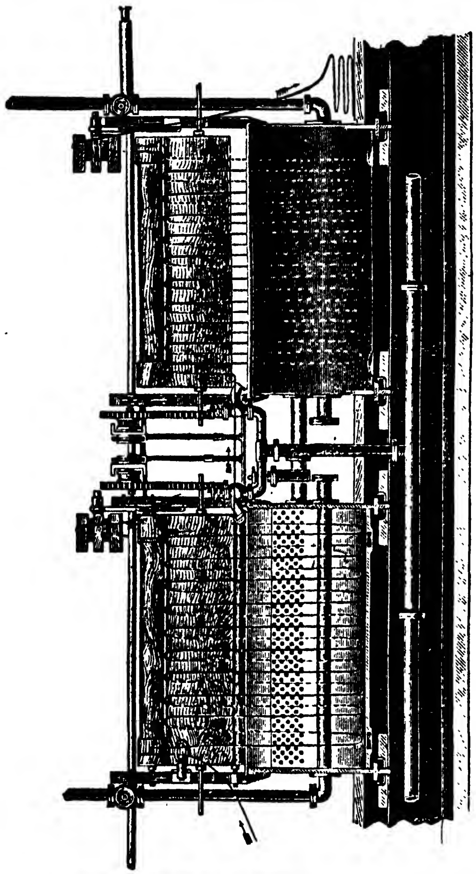


Fig. 74.

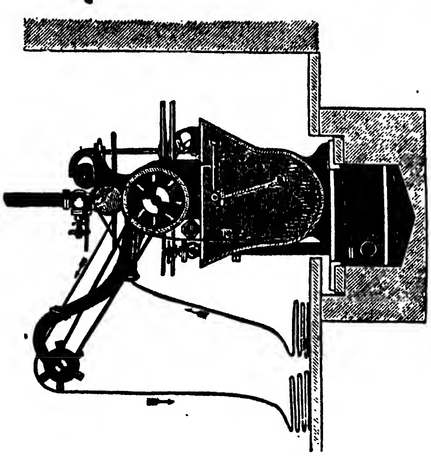


Fig. 75.

Spiral soaping becks (Mather & Platt).

The great convenience of the open soaping range for styles of work in which several operations can be performed in unbroken succession is best illustrated by the following outline descriptions of the most common applications to which it is put:—

Fixing or Raising and Soaping.—For this purpose the first cistern (that on the right) is charged with a solution of tartar emetic or other salt; the second with hot water; the third and fourth with soap; the fifth with clean fresh soap or water; and the sixth with water again. The cloth passes through the first cistern, and then between the squeezing bowls into the washing and soaping cisterns successively; out of the last of these latter it passes through the squeezer bowls into the final washing beck, and thence through the last mangle directly on to the drying machine.

Indigo Discharging or Cutting.—In this case the same series of operations is gone through, except that the first cistern is filled with cutting liquor—a solution containing sulphuric and oxalic acids.

Chroming Aniline Blacks and Raising Lead Yellows.—For this class of work the first cistern contains a hot solution of bichromate of potassium, and the other cisterns water and soap.

Developing Naphthol Colours.—In the absence of a special machine for this style, the open soaper may be utilised with advantage, but care ought to be taken to avoid filling the first cistern too full of the diazo solutions, since

these rapidly decompose, and not only become useless, but spoil the work past repair. For this reason, therefore, it is advisable to attach a smaller and portable cistern or trough to the open soaper, so that a constant supply of fresh diazo solution can be kept up without any undue waste of material. The cloth, prepared with β-naphthol and printed in suitable resists, is first passed through the diazo solution, wherein the background is instantaneously dyed, and then in succession through the washing and soaping cisterns, after which it is ready for drying and finishing.

Manganese Bronze.—In developing or raising these colours in the open soaper two methods may be adopted at will: either the first cistern may contain a solution of caustic soda and the second a solution of bleaching powder, or the first cistern alone may contain a mixture of the two. In either case the course of the cloth is as already described, *i.e.* through water and soap. If Engler's process for Manganese bronze is employed, the raising solution consists of an ammoniacal solution of bichromate of potash, or a mixture of the chromates of potassium and ammonium.

Prussian Blue may also be raised in a similar way with suitable iron salts, but in this case the soap must be replaced with water, since Prussian blue is destroyed by hot soap solutions.

The heating of the various liquors, water and soap solution, is effected by means of steam pipes, and the whole machine is driven by bevel gearing connected through a clutch to any suitable engine or motor. The soap solution enters the machine at the end opposite to the cloth, and therefore the latter, in its passage, always meets with a cleaner solution.

(2) THE SPIRAL SOAPING MACHINE is based upon the same principle as the spiral dye beck, and is worked in the same way, except that the cloth passes straight through it or through a series of soap becks arranged together. The soap enters the last beck first and overflows into the others, so that, as in the open soaper, the cloth passes forward through a cleaner and cleaner solution, until it finally meets with perfectly pure soap as it nears the end of the process.

Figs. 74 and 75 represent sections of coupled spiral soaping becks.

Spiral soaping is a somewhat drastic operation, especially if conducted at the boil, and it is therefore only applicable to the fastest colours, such as dyed reds, chocolates, and purples, Vat colours, Azoic colours, Aniline black and steam Alizarin pinks, etc.

(10) CLEARING OR CHEMICKING.

It frequently happens that, however well they have been washed and soaped, printed goods still retain an unpleasant (and unsaleable) soiled appearance on their white parts. It is to remove this defect that clearing is resorted to. The machine used for this process consists of a padding mangle, a small steaming box, a water mangle, and a drying machine, the disposition of which parts is shown in fig. 76.

The cloth runs continuously through a weak solution of bleaching powder contained in the padding mangle A; then through the steam box B, where the action of the bleaching powder is assisted by the hot steam; and finally through the water mangle C, where it is washed, and over the drying cans D.

A method of clearing proposed by H. Koechlin was to print a solution of bleaching powder on the face of the cloth with a fine pin roller, and then immediately afterwards print a dilute acid over it with a second similar roller, but this process is not used now. It not only takes up the time of a printer who can be more profitably employed, but is not so reliable as the above method.

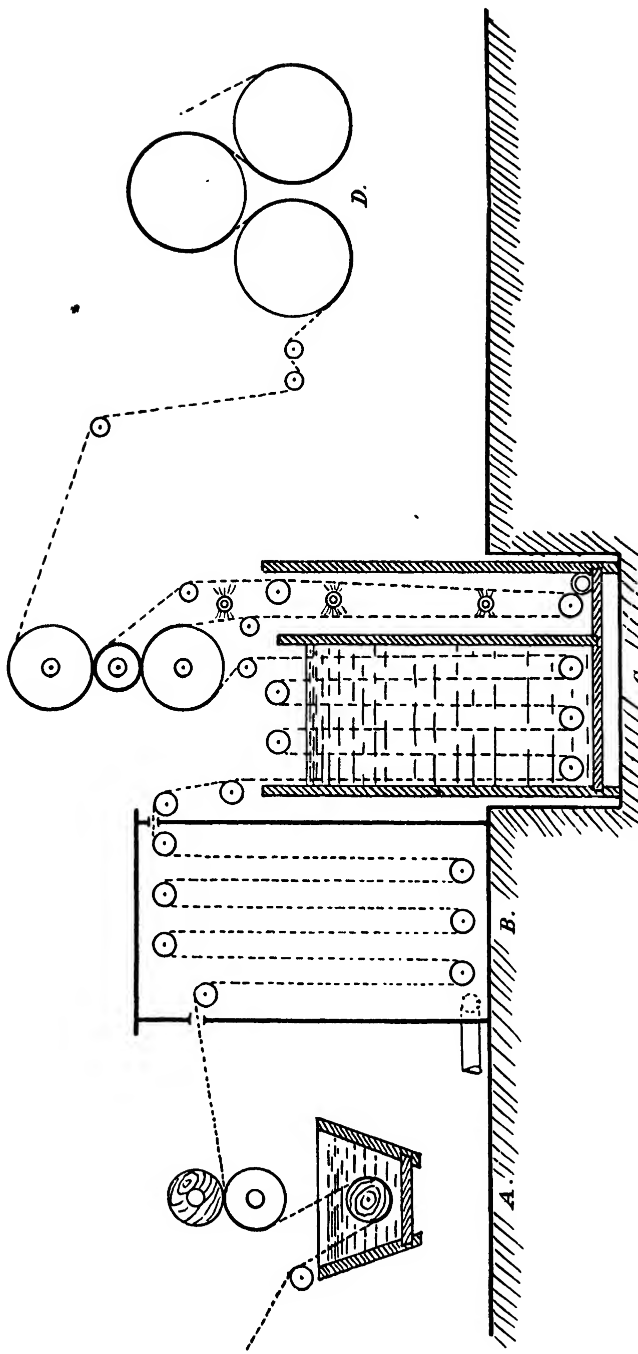
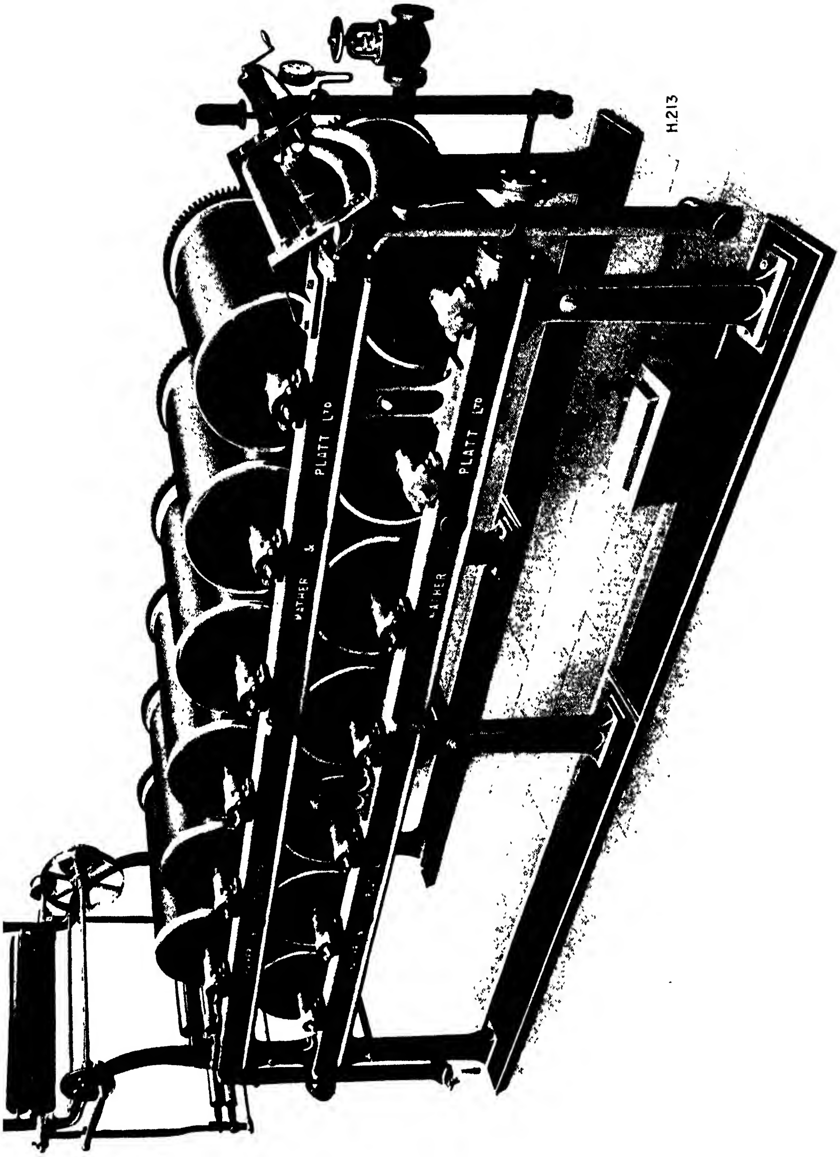


Fig. 76.—Section of chloring or chemicking machine.



Horizontal Drying Machine.

Another method of clearing printed goods is to mix a little bleaching powder solution with the stiffening materials used in finishing. This, however, is very rarely done, and at best is only a makeshift, yielding, on the whole, unsatisfactory results.

(11) DRYING.

Apart from hanging in heated chambers, a practice almost obsolete now except in Turkey-red works, the drying of printed goods is done in three ways: (1) over steam-heated drying cylinders, (2) by passing through hot air, and (3) on the stentering machine.

Drying over " cans " or cylinders is effected by means of the machine shown in Plate XIII., in which thirteen cans are shown.

This type of machine consists usually, however, of twenty-four copper or galvanised iron cylinders, heated by steam, and driven by bevel gearing from any convenient shaft or from a small engine. The journals of the cylinders are hollow, and revolve in stuffing boxes which form part of the hollow brackets bolted on to the hollow framework of the machine. In this way the interior of the cylinders communicates with the steam supply on one side of the machine and with the condensed-water outlets on the other. The steam enters the machine through the hollow uprights and passes into the cylinders by way of the hollow bracket bearings; inside each cylinder is an arrangement of so-called buckets, which catch the water of condensation and conduct it to the outlet journal of the cylinder through which it escapes, by way of the hollow framework at the opposite side of the machine, into a drain or tank.

Cylinder drying machines are made in various patterns; some like the one illustrated, some consisting of fewer tins or cylinders, and supported on a single pair of uprights, and others with any number of cylinders, arranged in two tiers horizontally, or, in several groups, vertically. The number of cylinders employed and their arrangement is merely a matter of convenience, depending on the weight of cloth the machine is intended for and the floor space available.

When cloth is impregnated with substances that are injuriously affected by coming in contact with the hot metallic surfaces of the cylinders, it is dried by being made to pass through a hot-air chamber or " hot flue." Formerly the hot flue was actually such, being a long, low, brick chamber, heated by a brick flue communicating with a furnace below. At the present time, however, this flue is seldom used; it has been replaced entirely by a system similar to that shown in Plate XIV—a system more convenient, more reliable, and in every way better. It consists of a large iron chamber through which the cloth passes over a series of guide rollers made of wood or brass. The chamber is heated by a combination of steam chests and a forced draught of hot air blown in by a powerful fan attached to a tubular heater, through which the air passes before entering the chamber.

Aniline black, naphthol prepares, padded mordants, and, in fact, all styles of work that would be injured by hard drying on hot cylinders, are dried in some sort of hot-air apparatus whenever possible. Failing such an apparatus, the best thing to do is to wrap the cylinders of an ordinary machine with several thicknesses of calico, and effect the drying with as little steam as possible.

Another system of drying, different from any of the foregoing, consists in drawing the pieces over and in contact with the surface of a series of double-convex copper steam chests. Whatever the merits of this system may be—and doubtless the drying is efficient enough—it is open to the objection that,

if the cloth is saturated with colour or has any colour penetrating through to the back, the colour in question is almost certain to smear badly during its progress over the chests. For lightly printed patterns it is possible that this method of drying is both rapid and economical, but, taken altogether, it is not so generally useful as those machines upon which all classes of goods can be treated.

The output of drying machines of any type depends upon the amount of water contained in the goods to be dried. It is important, therefore, that they should be freed as far as possible from all surplus water. In the case

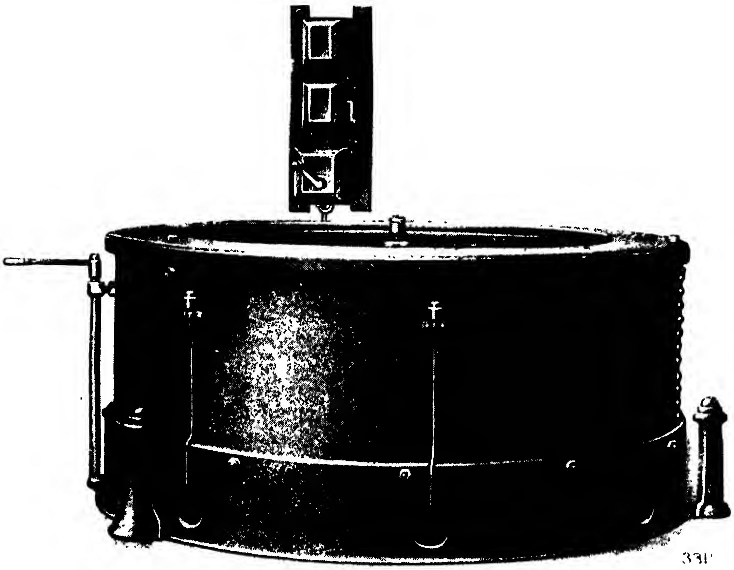


Fig. 77.—Hydro-extractor, electrically driven.

of white cloth this object is attained by passing the cloth between the squeezing bowls already described, but if printed goods were so treated the colours might mark-off. To avoid this, use is made of the hydro-extractor, a machine in which all excess of water is driven out of the cloth by centrifugal force. (See fig. 77.)

The hydro-extractor consists of a strong circular cage of iron or copper supported on a central pillar, so that it is capable of revolving at a high speed when actuated by a small engine or electric motor. The cage is enclosed in an outer casing of cast iron, which prevents the water from splashing over the floor and the neighbouring machinery. The cloth to be hydro-extracted is loosely bundled up in comparatively small lots, and packed evenly in the cage so as not to upset its balance; the engine is then set in motion, and the water is forced out of the goods by the enormous centrifugal force generated by the high speed of the revolving cage (1500-2000 revolutions per minute).

Even the hydro-extractor can only be used for the fastest colours, and only then after a thoroughly good washing and soaping. Dyed Alizarin colours (Madder style), Aniline black, and a few other colours can be safely treated in the extractor; but most steam styles and discharges and resists in colours,

are apt to, and in most cases do, mark-off, and must be squeezed in the open width before drying—not in the rope or the bundle forms.

The various conveniences attached to all calico printing machinery—such as scrimp rails, opening rollers, tension bars, scutchers, etc.—are so numerous, and vary so greatly in construction, that it would be impossible to go into a full explanation of their varied uses. Moreover, they are merely contrivances for doing away with hand labour of a simple sort, and do not form any essential part of the machines to which they are attached, although, at the same time, they add greatly to their efficiency as machines. It may be noted that scrimp rails are corrugated bars, with the corrugations diverging from the centre; the cloth in passing over them tends to run in the grooves and is stretched in consequence; that opening rollers and cones are similar in construction, but revolve, either with or against the cloth; that tension rails are a series of bars, between which the cloth is threaded in such a way that it passes over the first, under the second, over the third, and so on, under and over the whole series, until it becomes sufficiently taut to enter the printing or padding machines, etc.; and that "scutchers" are devices for opening out the cloth from the rope state to its full width: this they do by beating a long length of rope as it passes over them, shaking it out and untwisting it so that as it passes over a pair of spiral opening rollers, some distance from the revolving beater, it becomes opened out to its full width.

For further particulars of these and other minor devices for increasing the automatic capabilities of the various machines used in washing, dyeing, and drying, reference must be had to treatises dealing more especially with the mechanical aspect of textile colouring, or to *A Manual of Dyeing*, by Knecht, Rawson, and Loewenthal, in which is described the most important machinery employed for the above purpose.

PART VI.

MORDANTS, ETC.

MORDANTS, ETC.

So enormous is the number of colouring matters now at the disposal of the calico printer, and so diverse are their chemical and physical properties, that, as might be expected, different classes of them affect the fibre in very different ways. Some colours—those belonging to the direct dyeing class—possess in themselves the power of dyeing textile fabrics more or less permanently; others, like the basic aniline and the acid dyestuffs, also possess this power as regards the animal fibres, wool, and silk, but have scarcely any affinity at all for the cotton fibre, unless the latter is prepared with some substance capable of precipitating the colour upon it in the form of an insoluble lake; and yet other colouring matters (more correctly colouring principles, for any colour they may possess is of no practical value) can only be applied to the fibres in combination with certain metallic salts or oxides which unite with them to form intensely coloured and very insoluble lakes, which, being produced in the body of the fabric, are in most cases exceedingly fast to light, air, water, and soap.

The difference in the behaviour of different colouring matters towards the cotton fibre is readily exhibited in the following simple printing trials:—

(1) Print on a piece of plain, bleached calico three stripes, consisting respectively of a thickened solution of (*a*) Erika (direct dyestuff), (*b*) Magenta (basic dyestuff), and (*c*) Alizarin (mordant dyestuff). Steam the cloth for an hour. The Erika and Magenta will be found to give a pink stripe, while the Alizarin remains yellow. Now wash and lightly soap the cloth; the Magenta and the Alizarin are almost entirely removed, whereas the Erika is but little affected, thus showing that it alone has dyed the cloth permanently. It is not a very fast colour, but still it is capable of dyeing cotton without any addition.

(2) Now add to the Magenta printing colour a little tannic acid, and to the Alizarin a little acetate of alumina. Again print them on white calico and steam for an hour, when both colours will yield a pink. Divide the cloth into two parts, and treat *one-half* in a solution of tartar emetic. Then wash and soap the two pieces together, dry them, and compare them with each other, and also with the first trial. It will be at once evident that the Magenta and Alizarin are now fixed upon the fibre in such a way as to resist soaping; and further, that the Magenta on the half of the second trial, treated with tartar emetic, is more resistant than that on the untreated half, whereas the Alizarin is equally fast in both cases, and remains practically unaltered in all respects.

This experiment shows (1) that some dyestuffs require the addition of other bodies before they can be fixed upon the cloth; (2) that in the case of colours like Magenta (basic aniline colours) a special treatment with a metallic salt is necessary before the colouring matter can be properly fixed—that is, converted into its most insoluble state; and (3) that the tinctorial properties of bodies belonging to the Alizarin family—bodies which when used alone possess no powers of dyeing any fibre—can only be utilised when they are combined with a suitable metallic base which not only unites with them to form a highly

coloured, insoluble body or lake, but also has the effect of fixing this lake firmly upon the fibre.

The tannates of the colour-bases of Magenta and similar colours, are only partially insoluble in soap solutions; hence the necessity for treating them in a solution of tartar emetic which fixes the tannic acid upon the cloth as a very insoluble metallic tannate.

(3) Print two separate pieces of cloth, the one with four Alizarin colours, containing respectively the acetates of alumina, chrome, tin, and iron, and the other with four Magenta colours, containing, in like manner, tannic acid, aluminium acetate and a solution of arsenious acid in glycerine, and albumen, or any other mordant or fixing-agent whatever. After steaming, all the Magenta colours will be found to have yielded more or less the same shade of red, while the Alizarin colours will have given four distinct colours, namely, red, claret, orange, and purple, or, if the acetate of iron was strong enough, a deep-purplish black.

(4) Again, print a piece of white calico in stripes of aluminium, iron, chromium, and tin acetates; pass through the rapid ager, and fix in a weak solution of ammonia. Dye three separate portions of the cloth thus printed in Erika, Magenta, and Alizarin respectively. The Erika will dye the cloth *all over* in pinks of varying intensity and brightness; the Magenta will only dye the printed parts in different shades of red or pink; but the Alizarin will have dyed the same printed parts in full deep shades of red, purple, claret, and orange—shades so fast that they may be severely soaped until the unprinted parts of the cloth are almost white, or at least as free from dye-stains as hot soaping will make them. Treated in the same way, the Magenta and Erika colours would be entirely removed.

Analogous results are obtained when wool or silk are substituted for cotton, or when Logwood, Quercitron bark, etc., are substituted for Alizarin. The colours produced are, of course, different, and they act differently on the different fibres, but the effects obtained are quite as various and distinct as the above, and demonstrate quite as clearly the necessity for treating all colours according to their chemical properties, and according to the nature of the material to which they are to be applied.

From these four experiments it is clear that Erika, Magenta, and Alizarin represent, broadly, three quite distinct classes of colouring matters: (1) those possessing an inherent affinity for the cotton fibre; (2) those which can only be fixed upon it by means of other substances, and even then only yield various shades of one colour; and (3) those which require to be combined with a metallic base, and yield different colours with different bases.

The first and second classes have two qualities in common; they both consist of bodies in which the colour exists as such, and they both dye the fabric in one colour only, which is merely fixed thereon in an almost unchanged state, —in the case of basic colours, tannic acid simply replacing acetic or hydrochloric acid, etc., as the case may be. Such bodies have been aptly termed *monogenetic colouring matters* by the late J. J. Hummel; while such as Alizarin, Logwood, etc., which possesses no colouring power in themselves, but yield various coloured precipitates with different bases, are known as *polygenetic colouring principles.*

Although, generally speaking, each class of colouring matters is applied in a special way, it is none the less difficult to draw a hard-and-fast line between the different groups. Some colours possess the qualities of one, and are applied by the methods of another, and others, again, form a class by themselves. On the whole, then, the simplest and most practical classification is that based upon the methods and means of application; and as many of the mechanical

operations employed for this purpose are common to many colours, it is possible to group the latter into styles—a term which includes everything connected with the production of a given kind of calico print.

As already observed, this question of style is largely, if not entirely, a question of the behaviour of colouring matters towards the fibre; but, from what has just been said, it will be evident that some classes of colouring matters have no action whatever upon the cotton, wool, or silk fibres, except in presence of certain other bodies which precipitate them as insoluble lakes. These bodies —such as tannic acid and various metallic salts, etc.—are absolutely essential to the development and fixation of colours in some styles of printing; and as they constitute an actual ingredient of the finished colour in many cases, and in others play an important part as oxidising or reducing agents, some idea of their composition, manufacture, and function is necessary to a proper understanding of the principles underlying each of the many styles of printing.

Such bodies as form insoluble compounds with colouring matters are known as *mordants*; all the others, which do not act as mordants proper, but which are used largely as oxidising, reducing, brightening, and cleansing agents, are known under various names, and may be classed as *assistants*.

MORDANTS.

By far the greater number of the fastest colours known, though capable of solution or suspension in water and other solvents, and of penetrating in this state into, and staining the fibres of, various textile materials, do not alone possess the property of attaching themselves thereto so permanently as to withstand the action of hot soap solutions or of light and air. In order to render them capable of resisting these influences, they must be combined with mordants, or otherwise converted into insoluble bodies.

Mordants are a numerous class of substances. They comprise acids, neutral salts, basic salts, and hydroxides, and may or may not possess colour. In any case their colour is not an essential feature, their sole use being to precipitate the colouring matter upon the fibre in an insoluble state. To this end they are applied in various ways, according to their nature, to the state of the fibre under treatment, and to the style of work in hand. In calico printing they are either precipitated and fixed upon the cloth previous to dyeing (dyed style), or they are applied to it, by printing, at the same time as the colour (mixed with it, in fact), the printed cloth being afterwards steamed, during which process the mordant is decomposed, and, under the influence of the heat and moisture, its metallic base combines with the colouring matter to form an insoluble compound, which is deposited within the fibres of the cloth, and fixed there more or less permanently at the same time.

In wool and silk printing this latter process is also employed, but the method of mordanting these animal fibres is quite different and much simpler than that of mordanting cotton, which is a particularly inert substance, and has but little natural attraction for most mordants.

In mordanting wool, it usually suffices to boil it in dilute solutions of metallic salts, containing either free sulphuric, formic, lactic, and other acids, or acid salts like bisulphate of soda and cream of tartar. Under the combined action of heat, dilution, and of the acid additions, the mordanting salt, in presence of the wool, dissociates, and its base, or at least its metallic constituent, unites with the fibre in some way that, up to the present, has not been definitely ascertained.

Silk is mordanted in the same manner as wool, except that it is rarely heated beyond tepidity. It possesses the property of absorbing metallic salts (especi-

ally if they be at all basic) from cold concentrated solutions, and these salts, which it takes up in a more or less unchanged condition, are subsequently dissociated when the silk is washed in water. Hence silk is usually steeped in strong solutions of various basic salts, then squeezed and washed in water, the mere dilution with which is sufficient to bring about the dissociation of the salt, and to precipitate it in and upon the fibre in a still more basic and insoluble form.

Cotton, on the other hand, requires much more elaborate treatment before it can be satisfactorily mordanted. Unlike silk and wool, it has no power of decomposing metallic salts by mere steeping and boiling in their solutions, nor does it possess any affinity for mordants, except tannic acid, which it absorbs readily and retains fairly tenaciously. In mordanting cotton, therefore, the aim is to precipitate insoluble bodies within the substance of the fibre, and when this is successfully accomplished the fibre retains them almost as firmly as if they were chemically combined with it.

The salts used by the calico printer for mordanting cotton comprise (1) those which are easily dissociated by exposure to warm, moist air after printing; (2) those which form insoluble salts with various acids; and (3) those the metallic bases of which precipitate certain colouring matters as insoluble lakes, under suitable conditions.

To the first class belong the acetates, sulphate-acetates, and basic acetates of alumina or iron. The cotton is impregnated with their solutions, dried, and exposed to warm, moist air in an ageing apparatus. The greater part of the acid is driven off during this process, leaving a basic salt on the fibre. Any remaining acid is then neutralised by ammonia, chalk, etc., or replaced by an acid such as phosphoric, silicic, arsenic, or in some cases tannic acids, which precipitates the iron or alumina. With the exception of the last mentioned, these acids are employed in the dunging process as salts of sodium.

To the second class belong mordants like basic ferric sulphate, basic sulphates of alumina, and various chromium salts, any of which can either be precipitated by tannic acid, arsenates, phosphates, or silicates, or simply be converted into hydroxides by alkalies and sodium carbonate.

The third class includes all salts whatsoever that are used in the so-called steam styles. The mordant and colouring matter are mixed together and printed on the cloth, which is then subjected for an hour or so to the action of steam, as already described (see Steaming). In the cold, the mordant and colouring matter do not react upon each other; but under the influence of hot steam the former decomposes, its acid or acids are liberated, and its base combines with the latter, which it precipitates as an insoluble coloured lake in the body of the cloth. Amongst the most important mordants of this class are the acetates of alumina, iron, chrome, tin, zinc, and nickel, the nitrates, citrates, and sulphocyanides of aluminium, zinc sulphate, oxalate, and even hydrate, of tin, acetate of lime, and various other salts and double salts which act in the same or similar ways.

On the whole, the acetates are the most generally useful of all mordants. They are stable in the cold (many of them can be boiled without decomposing if they are not too basic); their acid is readily removed in ageing and steaming, or in dunging, and other after-treatments; and, above all, they neither tender the fibre nor does the liberated acid injuriously affect the colours. The same may be said of the formates, but hitherto these salts have found but occasional use in practice, though they are well worthy of more attention, since in many cases they give brighter colours than the corresponding acetates. Nitrate of alumina is chiefly employed to impart a more fiery tone to Alizarin reds, and most other special salts are used for obtaining some particular effect,

or in cases where experience has shown that they are the most suitable for the purpose intended.

In mordanting cotton with acetates of alumina and iron it generally happens that only a portion of the acetic acid is driven off in ageing, the residue remaining in the cloth as a soluble basic acetate, or even as a normal acetate, either of which would dissolve off in the dye bath and cause stains if allowed to remain. In order, therefore, to remove the last traces of acid, the cloth is dunged either in ammonia, carbonate of soda or chalk, or in phosphate, arsenate, or silicate of soda. If the first three are used, the mordant exists on the cloth as a hydroxide; if the latter three, as a basic salt, or a mixture of basic salts and hydroxide. In any case it is insoluble, and thus gives rise to no bad work during the subsequent dyeing operation.

Cow-dung, when used as a fixing agent, produces the same effect as the above substances, and for printed mordants is by far the most effective of this class of bodies, since it not merely precipitates the unchanged mordant, but removes at the same time, and very rapidly, the thickening material that has been used in printing.

When mordants are printed on calico, a good deal more is applied than the cloth is capable of absorbing; the result is that the excess adheres loosely to the surface of the cloth, and, if not removed by a thoroughly good dunging, will combine with the colouring matter in the dye bath and form a superficial crust or colour lake, which not only obstructs the penetration of the dye liquor into the body of the cloth, thus preventing the latter from being properly dyed, but also causes immense damage by rubbing off on to the unprinted portions of the cloth, which are intended to remain white. Moreover, when such imperfectly dunged pieces are soaped after dyeing, the surface crust of colour washes off in patches, leaving the goods in an unsaleable condition, owing to their irregularity in colour.

Although most mordants are applied as neutral, or slightly acid, solutions of various salts, they may also be applied in alkaline solution in all cases where the base is either soluble in caustic soda, or where it plays the part of an acid, *e.g.* stannate of soda, aluminate of soda, plumbite of soda, and alkaline iron, and chrome mordants. When applied in this way they are usually fixed in a bath of weak mineral acid, or passed through a salt which neutralises their alkalinity—ammonium chloride, for example—or by being allowed to decompose spontaneously in contact with the fibre, and afterwards washed in water. Most alkaline mordants are only stable in strong alkaline solution, and even then are very liable to spontaneous decomposition: dilution with water, therefore, precipitates the dissolved oxides, and acts as a veritable fixing process when applied in the form of wash-water.

Mordants are not confined to metallic compounds, for, strictly speaking, any substance that is fixed upon the fibre in combination with a colouring matter is a true mordant—that is, if it forms an essential constituent of the colour lake. In this connection β-naphthol, tannic acid, and oleic and other fatty acids are all, in a sense, mordants, since they are all important agents in the development and fixation of an enormous number of colours on the cotton and other fibres. It is true that tannic acid and the fatty acids are usually present on the fibre as metallic salts in most cases, but their metallic bases are not necessarily their essential features, and usually act as mere fixing agents, or at most are introduced for the purpose of making the final colour lake more complex—it being a general rule that the more complex the lake the faster the colour. The property possessed by the tannic and fatty acids of combining with metallic bases is utilised in many styles of printing. For instance, goods printed in aluminium acetate are frequently dyed, after ageing and dunging.

in a solution of tannic acid, and can then either be dyed up again in Alizarin, or treated in the same way as goods mordanted in tannate of antimony, namely, dyed up in any basic aniline dyestuff. Similarly, fatty acids in the form of sodium salts are combined with alumina mordants in Turkey-red dyeing, and are absolutely essential to the production of a fine, bright, fast red.

At the same time, cloth prepared in either pure oleic acid, or oleate of tin, lead, alumina, etc., can be dyed in many artificial dyestuffs. The shades obtained in this way are very bright, but will not stand much washing.

The great variety of mordants, together with the great diversity of their chemical and physical properties, makes it impossible to formulate any general rule for their application to the fibre. At all times they must be chosen and applied with due regard to the nature of the colouring matter and material to be dealt with; and as each individual colouring matter possesses its own characteristics, these will, to a great extent, determine the mode in which it is to be fixed. Then, too, the appliances at hand modify in many cases the composition and application of mordants, and must therefore be taken into account if the best results are to be secured. Very often the process of drying adopted makes all the difference between success and failure: a mordant or a colour that comes out satisfactorily when the cloth is dried in hot air may be utterly ruined if the drying is done on steam-heated cylinders. In such cases the composition of the mordants, etc., must be modified in order to adapt them to the altered conditions; so that, quite apart from all other questions, that of machinery enters largely into all calculations respecting the production of a given effect.

As a rule, the drying of cloth impregnated with mordants that readily dissociate should be conducted at as low a temperature as possible: if dried too sharply, the mordants are apt to become *dehydrated* (technically " burned "), and in this state they yield exceedingly poor colours on dyeing.

It is important, too, that aluminium and iron mordants should be aged *gradually*, and under suitable conditions of temperature and humidity, otherwise they fail to penetrate the fibre sufficiently. The mordant lies on the surface of the cloth, and any colour dyed on it afterwards is thin and uneven, lacks body and brightness, and, above all, is not fast to soaping, during which operation it runs or marks-off when the goods are squeezed or wrung out.

Iron mordants used for the dyed style of printing are especially sensitive to high temperatures in drying and ageing, and require the most careful treatment after printing to prevent them from oxidising too rapidly.

Some mordants act as such by virtue of their acids, others by virtue of their bases: the former are fixed by means of metallic salts whose bases form insoluble salts with them, and the latter either by alkalies which precipitate them as hydroxides and basic salts, or by salts with whose acids they combine to form insoluble salts.

In the following account all the more important mordants and assistants used by the calico printer are given, together with a brief description of their preparation, modes of application, suitability for special purposes, and behaviour under varying conditions.

(1) Aluminium Mordants.

Salts of aluminium were known to and used as mordants by the Hindoos, Chinese, and Egyptians in very early times; and their value is such that at the present time they still constitute perhaps the most generally useful group of this class of bodies. They are cheap, easily prepared, and can be applied to all fibres.

Alum.—Alum comes into the market in two forms, viz. *Potash Alum* [$K_2Al_2(SO_4)_4.24H_2O$], containing 10·8 per cent. of Al_2O_3, and Ammonia Alum [$(NH_4)_2Al_2(SO_4)_4.24H_2O$], containing 11·9 per cent. of Al_2O_3. The importance of the alums has been diminished considerably by the introduction of a comparatively pure aluminium sulphate, $Al_2(SO_4)_3.18H_2O$, but they are still preferred by some calico printers on account of their regular composition and high state of purity.

Application.—The application of alum to the cotton fibre depends upon the fact that when cotton is impregnated with basic aluminium sulphate and then dried, a more basic, and more or less insoluble, salt is precipitated upon it.

The basic salts are made by adding varying quantities of sodium carbonate or bicarbonate, chalk or hydrate of alumina to solutions of the normal salt. The degree of basicity desired may be obtained by working according to the following equations:—

(1) $K_2Al_2(SO_4)_4 + 2NaHCO_3 = Al_2(SO_4)_2(OH)_2 + K_2SO_4 + Na_2SO_4 + 2CO_2$.

(2) $2K_2Al_2(SO_4)_4 + 6NaHCO_3 = Al_4(SO_4)_3(OH)_6 + 3Na_2SO_4 + 2K_2SO_4 + 6CO_2$.

(3) $K_2Al_2(SO_4)_4 + 4NaHCO_3 = Al_2(SO_4)(OH)_4 + 2Na_2SO_4 + K_2SO_4 + 4CO_2$.

The behaviour of these salts varies considerably on boiling and dilution. Solutions of the normal salts are unaffected, but the more basic they are made the more readily do they dissociate. For instance, according to Liechti and Suida, the basic salt $Al_4(SO_4)_3(OH)_6$ begins to dissociate at 68° C., or when diluted with water to three times its original volume, and when dried on the cotton fibre it gives up to it 58 per cent. of its alumina. The salt $Al_2(SO_4)_2(OH)_2$ is much more stable; it can be diluted with fourteen times its volume of water or be boiled for half an hour before it commences to deposit a more insoluble basic sulphate and yields 50 per cent. of its available alumina to the fibre. The normal salt only yields 13 per cent. of its alumina to the fibre, and consequently is of little value except as the raw material for the manufacture of other mordants.

The presence of potassium and sodium sulphates in basic aluminium sulphate solutions increases their liability to dissociate on boiling, but in the case of the salt made according to the first equation the precipitate re-dissolves on cooling.

Basic sulphates of alumina are only used by the calico printer for Turkey-red dyeing, other salts being found much more suitable for printing by roller or block.

The cloth is slop-padded in the basic mordant, then dried and fixed in either carbonate of ammonia, phosphate, silicate, or binarsenate of soda, or in ammonia. It is then well washed, and may be dyed up in any suitable colour.

In Turkey-red dyeing the usual procedure is first of all to impregnate the cloth with an oil mordant; then pass it through a solution of basic sulphate of alumina corresponding to the formula $Al_2(SO_4)_2(OH)_2$ and dry it. The oil and alumina mutually fix each other on the fibre, and the resulting red is much more brilliant than if no oil entered into its composition. Turkey-red dyeing will be described later.

The first method of fixing may be employed for dyestuffs other than Alizarin, although this can be equally well dyed up in the absence of oil, yielding on subsequent oiling and steaming a very bright and fast red.

The deposition of alumina from basic sulphates can also be effected by ageing; but this method is rarely adopted in practice, since the liberated acids are apt to tender the fibre unless it contain oil; besides which, ageing offers no advantages over other methods of working.

A basic sulphate in use at one of the most important Turkey-red dyeing establishments is made as follows:—

$\begin{cases} \text{30 kilos. of potash alum.} \\ \text{300 ,, boiling water.} \end{cases}$

Dissolve and add gradually, stirring all the time—

$\begin{cases} \text{10 kilos. soda crystals } (Na_2CO_3.10H_2O). \\ \text{100 ,, water.} \end{cases}$

Allow to cool, and set at 8° Tw.

Cloth prepared in a solution of sulphated oil equal to 5 per cent. fatty acids is run through the above basic sulphate at 32° C., then dried and stored until required for dyeing in Alizarin. Just before dyeing, any unprecipitated alumina is finally fixed on the cloth by a passage in open width, through a series of dunging becks containing a weak solution of sodium binarsenate and chalk. It is then washed and entered into the dye bath.

Other basic sulphates of alumina may be used in a similar way.

Sulphate of Alumina.—This salt $[Al_2(SO_4)_3.18H_2O]$ occurs in commerce in the form of irregular lumps, having a granular surface and of a fused appearance. It was originally manufactured from bauxite, and used to contain an appreciable amount of iron. It also varied a good deal in composition, and on these two counts it was regarded with disfavour by most calico printers of a few years ago. At the present time, however, it is prepared on the large scale from the alumina obtained as a by-product in the manufacture of soda from cryolite. This alumina is practically free from iron, and when dissolved in sulphuric acid and evaporated down it yields a remarkably pure sulphate of alumina.

Aluminium sulphate has two advantages over the alums. In the first place, it contains more alumina (15·5 to 19 per cent.); and in the second, it is entirely free from the sulphates of potash and soda, which are not only useless but add to the cost of production. It also contains less water in proportion to its percentage of alumina, so that, taken all together, it is much cheaper as a raw material than either of the alums.

Basic sulphates of alumina are made from the normal commercial sulphate in exactly the same way as they are made from alum; but since less sodium and potassium sulphates are present, they are somewhat more stable, though, when heated and diluted, they produce precipitates analogous to those already mentioned.

The mordants made from aluminium sulphate are applied to cotton in the same manner as the basic alums. They are also largely used for the mordanting of wool and silk by the ordinary methods. It is usual, however, to employ the normal salts for wool, the basic sulphates being apt to go on the fibre irregularly.

Acetates of Alumina.—These salts are the most important to, and are most largely used by, the calico printer. They are easily prepared, either by dissolving the hydrate in acetic acid or by the double decomposition of aluminium sulphate and lead acetate:—

$$Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 = Al_2(C_2H_3O_2)_6 + 3PbSO_4.$$

Solutions of the normal salt always smell of acetic acid, and this fact led Crum to assert that its real composition was $Al_2(C_2H_3O_2)_4(OH)_2$, which body remains when solutions of the normal salt are evaporated to dryness under reduced pressure and at a low temperature. He regarded the solution as containing the free acid.

Normal acetate of alumina is neither decomposed by boiling nor by dilution, but it deposits the hydroxide on standing for a long time; and, in common

with the basic acetates, it is precipitated when boiled in the presence of sulphates, whether of alumina, soda, or potash. On cooling, however, the basic salt precipitated re-dissolves in the case of the normal acetate, whereas in the case of the basic acetates it does not.

In preparing aluminium acetates for printing it is usual to leave a portion of the aluminium sulphate undecomposed. The presence of a soluble sulphate prevents the solution of lead sulphate which is dissolved in appreciable quantities by pure acetate of alumina. Where the pure acetate is found to give the best results or is essential, and where the presence of lead sulphate is detrimental —as, for instance, in steam Alizarin pinks—it can be prepared either by the double decomposition of acetate of lime and sulphate of alumina, or by dissolving aluminium hydroxide in acetic acid.

It has been found by experience that in most cases it is inexpedient to replace the whole of the sulphuric acid in aluminium sulphate by acetic acid; hence most of the acetates technically known as "red liquors" are strictly speaking *sulphate-acetates*.

The sulphate-acetates, besides being cheaper than the normal acetates, are better in that they give up practically the whole of their alumina to the fibre during the ageing process. This is probably due to the fact, already noticed, that in the presence of soluble sulphates a basic salt is precipitated on heating, and as all the water has been driven off in the drying operation after impregnation or printing, this basic salt cannot re-dissolve, and so remains on the fibre in an insoluble state until it is finally fixed thereon permanently by the dunging process.

Basic acetates of alumina can be obtained by adding sodium carbonate, or bicarbonate, to the *normal salt*, in which case no soluble sulphate is present:—

$$(1)\ Al_2(C_2H_3O_2)_6 + 2NaHCO_3 = Al_2(C_2H_3O_2)_4(OH)_2 + 2Na(C_2H_3O_2) + 2CO_2$$

or

$$(2)\ Al_2(SO_4)_3 + 3Pb(C_2H_3O_2)_2 + Na_2CO_3 + H_2O = Al_2(C_2H_3O_2)_4(OH)_2 + 2Na(C_2H_3O_2) + CO_2 + 3PbSO_4.$$

It makes no difference to the ultimate result at what stage the sodium carbonate is added so long as there is sufficient lead acetate used to combine with the whole of the sulphuric acid in the aluminium sulphate—an acetate of soda is always in solution when this is the case.

If, however, one molecule of lead acetate is replaced by a molecule of sodium carbonate the same basic acetate of alumina is produced, but at the same time sodium sulphate is also a product of the reaction and remains in solution:—

$$Al_2(SO_4)_3 + Na_2CO_3 + 2Pb(C_2H_3O_2)_2 + H_2O = Al_2(C_2H_3O_2)_4(OH)_2 + 2PbSO_4 + CO_2 + Na_2SO_4.$$

The only difference between the results of the two sets of reactions is that basic acetates containing *sodium acetate* are not precipitated by dilution with water, whereas those containing *soluble sulphates* are so precipitated. Heat causes precipitation in both instances.

The basic sulphate-acetates are obtained in the same manner as the above, and act in the same way in most respects. On heating a basic sulphate-acetate it dissociates, but the precipitate re-dissolves on cooling if its basicity does not exceed that represented by the formula $Al_2SO_4(C_2H_3O_2)_3(OH)$.

The basic acetates and sulphate-acetates are only employed for dyeing, the best for this purpose being the last mentioned, viz. $Al_2(SO_4)(C_2H_3O_2)_3(OH)$, which is sometimes used to replace basic sulphate of alumina in mordanting for Turkey-red.

Many other basic acetates and sulphate-acetates can be prepared by adding calculated amounts of various alkalies. The normal sulphate-acetates are simply made by using a deficiency of lead or calcium acetate, and can be varied in composition as occasion dictates:—

$$Al_2(SO_4)_3 + 2Pb(C_2H_3O_2)_2 = Al_2(SO_4)(C_2H_3O_2)_4 + 2PbSO_4.$$

Most of the commercial red liquors are crude sulphate-acetates of alumina. They differ greatly in composition, no two makers adopting quite the same proportions, or even exactly the same ingredients. The value of a red liquor can only be determined by a practical trial; its analysis affords but the slightest of clues to its suitability for the given purpose, and consequently its behaviour can only be ascertained by the results it gives on a practical basis. What is known as tin red liquor approximates closely to a true normal acetate, though it possess the reddish-brown colour of all red liquors—a colour they derive from the presence of organic matter in the crude calcium acetate, from which they are usually manufactured.

That the composition of red liquors varies within wide limits is shown by the following formulæ, all of which represent "receipts" that are or have been used in practice:—

	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.
Water	1740	2000	1500	1000	1000	1000	1200	..	..	3600
Lead acetate (brown)	660	1140	945	400	400	300	500	..	..	1590
Potash Alum	..	..	..	400	400	400	600	..	400	1908 (or 1336)
Sulphate of alumina	600	665	665	..	..	..	..	70	..	
Sodium carbonate (10 aq.)	..	..	..	40	..	35	..	..	..	150
Chalk	..	..	..	..	35	..	..	7	25	..
Calcium acetate 24°Tw	..	..	..	..	..	..	..	250	1000	..
	1	2	3	4	5	6	7	8	9	10

Of the above, Nos. 1, 3, 4, 5, and 10 are perhaps the most reliable in practice, though the most basic are only suited to mordanting by slop-padding in a mangle, since they would be liable to dissociate if boiled up with thickenings for printing. For the latter purpose Nos. 1 and 3 are the most useful, and both have given good results on the large scale, when printed, aged, etc. No. 4 without the soda also yields excellent results, and was at one time used very largely in England under the name of "4/4 liquor."

Aluminium acetates play an important part in the steam style of printing. In a steam Alizarin red, for instance, the mordant is simply added to the thickened Alizarin, upon which it does not act in the cold. When printed on calico, however, and steamed, it decomposes, combines with the Alizarin to form a red lake, and at the same time fixes this lake on the fibre.

A good aluminium acetate for steam work is made as follows:—

Dissolve 60 kilos. of sulphate of alumina in 174 kilos. of water.

Then add—

66 kilos. *white* lead acetate.

Stir until the lead salt is dissolved; allow to settle, and then decant the clear liquor, which will stand at about 15° of Twaddell's hydrometer. The precipitated sulphate of lead is washed twice with 80 litres of water each time,

and as the wash-waters contain a large amount of aluminium acetate they are saved and utilised for the preparation of the next batch, for which smaller amounts of alum and lead salts are taken, viz.—

$$\left\{\begin{array}{l}160 \text{ litres of weak } Al_2(C_2H_3O_2)_6 = \text{(wash-waters).}\\ 14 \quad ,, \quad \text{water.}\\ 50 \text{ kilos. sulphate of alumina.}\end{array}\right.$$
55 ,, acetate of lead.

Nitrate-acetates of alumina are also used extensively in calico printing for giving a more brilliant and fiery tone to Alizarin oranges and scarlets. Either of the following recipes may be employed in their preparation:—

(1) $\left\{\begin{array}{l}200{\cdot}0 \text{ kilos. water.}\\ 133{\cdot}4 \quad ,, \quad \text{sulphate of alumina.}\end{array}\right.$
157·2 ,, acetate of lime 23° Tw.
177·2 ,, nitrate of lime 66° Tw.
Settle, and decant the clear liquor.

(2) NITRATE-ACETATE OF ALUMINA.
$\left\{\begin{array}{l}6{,}670 \text{ grms. of sulphate of alumina dissolved in}\\ 10{,}000 \quad ,, \quad \text{water, then add}\end{array}\right.$
4,000 ,, lead acetate.
2,000 ,, lead nitrate.
20,000 ,, water.
Settle, and decant.

The above sulphate-acetates and nitrate-acetates may be used for most purposes of calico printing in the steam style, but when steam colours are thickened with the natural gums—*e.g.* gum Senegal, gum arabic, etc.—it is often found preferable to make use of a pure acetate of alumina. This is prepared as follows:—

PURE ACETATE OF ALUMINA.
$\left\{\begin{array}{l}3000 \text{ grms. of aluminium hydrate 12 per cent. paste.}\\ 2000 \quad ,, \quad \text{acetic acid } 9^\circ \text{ Tw.}\end{array}\right.$
Warm until the hydrate is dissolved, then filter, cool, and set at 15° Tw.

ALUMINIUM HYDRATE.
$\left\{\begin{array}{l}66{\cdot}7 \text{ kilos. sulphate of alumina dissolved in}\\ 200 \quad ,, \quad \text{water and precipitated with}\end{array}\right.$
240 ,, caustic soda 23° Tw. (10 per cent. $NaOH$).
Wash the precipitated hydrate several times to free it from sodium sulphate, and then filter it until it contains 12 per cent. of dry hydrate.

Application of the Acetates of Alumina to Cotton.—These salts are not used at all in wool dyeing, and are only applied to silk (and wool) in printing. But for cotton they are employed more extensively than any other mordants in all branches of printing and dyeing, and are capable of yielding a great variety of effects. Cotton is most simply mordanted by their means, by being passed in the open width through their solutions, dried, and then aged and dunged as already described. For ordinary plain shade dyeing, however, they are rarely used, not because they are not suitable, but because they can be advantageously replaced by the basic sulphates of alumina, which are both cheaper to prepare and much more easily manipulated. On the other hand, the acetates and sulphate-acetates are the mordants *par excellence* for printing, since they may be applied in different ways, and in combination with many colours and other mordants.

The most important of their applications in printing is to the Madder style—a style in which the mordant is applied locally, as a pattern, and afterwards combined with Alizarin by dyeing. To produce this style (details of which will appear later) aluminium acetate thickened with starch, flour or British gum is printed on plain bleached calico, and dried, preferably in hot air, to avoid all risk of its being dehydrated or "burnt." The printed cloth is then aged under suitable conditions, and after dunging, to fix finally any unchanged acetate and to remove the thickening, it is dyed up in Alizarin, which only attaches itself to the printed parts of the cloth, leaving the rest white, or at most only tinted with an easily-removed stain. By varying the strengths of two or three printing colours that may be worked together in a multicolour printing machine it is possible to obtain shades varying from the darkest red to the most delicate pink; and by adding a little acetate of iron to the acetate of alumina in the red colour, any shade of maroon or chocolate can be added to the combination, each member of which is produced simultaneously during a single dyeing operation.

Alizarin is not the only colouring matter that can be used in conjunction with printed aluminium mordants. The vegetable colours—Persian berry, Quercitron bark, Logwood, etc.,—and artificial dyestuffs of the Alizarin group—*e.g.* Alizarin orange, Alizarin yellow, Gallopurple, etc.,—can be equally well applied in the dye bath. Even basic aniline colours may be successfully employed if the dunged cloth be previously dyed in a solution of tannic acid. The aluminium mordant in this case acts as fixing agent for the tannic acid, which is precipitated on the printed parts of the cloth as an insoluble tannate of alumina, and, as such, acts in every way as an efficient mordant for basic colouring matters of all descriptions—Methylene blue, Rhodamine, Auramine, Methyl violets, Methylene green, and Safranine.

For colours that are fixed and developed on the fibre by steaming, the value of the acetates, sulphate-acetates, and nitrate-acetates of alumina has been already noticed. For Alizarin red they are used in combination with other substances that are essential to the production of the brightest kind of red, and this is true also of their application to the fixation of other colouring matters. At the same time they play the part of true mordants in every case, and the various other additions are made for the sole purpose of modifying or increasing the brilliancy of the ultimate colour.

Red liquors are occasionally used to neutralise the acid liberated from Aniline black, but their suitability for this purpose is somewhat doubtful, seeing that aluminium chloride itself is dissociated under the influence of hot steam.

In Turkey-red dyeing the various red liquors are sometimes used instead of the basic aluminium sulphates, but they offer no particular advantages over them commensurate with the extra work entailed by the necessity for ageing and dunging.

Aluminium Nitrate [$Al_2(NO_3)_6$].—This salt is prepared by saturating nitric acid with aluminium hydrate, or by the double decomposition of aluminium sulphate and lead nitrate. The latter method is that usually adopted in practice.

ALUMINIUM NITRATE, 23° Tw.

$\begin{cases} \text{22 kilos. sulphate of alumina.} \\ \text{75 ,, boiling water.} \end{cases}$

Add gradually—

30 kilos. lead nitrate (finely ground).

Stir till dissolved, allow to settle, and decant the clear liquor. Set at 23° Tw.

Basic salts may be obtained in the usual way by adding calculated amounts of alkaline carbonates to the solution of the normal salt.

Nitrate of alumina is only used as a mordant for certain steam Alizarin red and oranges, to which it imparts a much livelier and more fiery tone than can be obtained from the use of any other alumina mordant.

The basic nitrates of alumina are not precipitated either on boiling or by dilution with water. They may be prepared in the following way directly, instead of working with the normal salt:—

BASIC ALUMINIUM NITRATE (Depierre):—

$$1\begin{cases}\text{1080 grms. potash alum (or 756 sulphate of alumina).}\\ \text{2000 ,, water.}\end{cases}$$

Add—

$$2\begin{cases}\text{1000 grms. water.}\\ \text{505 ,, bicarbonate of soda.}\end{cases}$$

Boil solutions 1 and 2 together and then add—

400 grms. nitric acid 64° Tw.

Make up to 10,000 grms. with water.

The above solution contains both sodium and potassium sulphates; its formula is $Al_2(NO_3)_3(OH)_3$, and it contains 1·6 per cent. Al_2O_3.

Aluminium Sulphocyanide.—This salt is prepared by the double decomposition of aluminium sulphate and barium sulphocyanide thus:—

$$Al_2(SO_4)_3 + 3Ba(CNS)_2 = Al_2(CNS)_6 + 3BaSO_4,$$

or by the similar reaction with $Ca(SCN)_2$, calcium sulphocyanide.

The following recipe has given excellent results on the large scale:—

$$\begin{cases}\text{8·5 kilos. barium sulphocyanide.}\\ \text{10 ,, water.}\end{cases} \qquad \begin{cases}\text{8 kilos. aluminium sulphate.}\\ \text{10 ,, water.}\end{cases}$$

Mix the two solutions together, stir well, allow to settle, and decant the clear liquor. If necessary, a little chalk may be added to neutralise any free acid that may be present.

Lauber recommends the following method, but it gives no better a product than the above:—

ALUMINIUM SULPHOCYANIDE.

$$\begin{cases}\text{5 kilos. aluminium sulphate.}\\ \text{5 ,, water.}\\ \text{250 grms. chalk.}\end{cases}$$

Dissolve and add—

11½ litres calcium sulphocyanide 30° Tw.

Settle, and decant the clear solution for use.

The basic sulphocyanides are not dissociated by mere dilution with water, but all, with the exception of $Al_2(CNS)_5(OH)$, decompose on boiling. The basic salts are not used in either dyeing or printing.

As a mordant for steam Alizarin reds and pinks, aluminium sulphocyanide is of paramount importance. Unlike the acetates and nitrates, it is not an acid salt; hence it does not take the doctor edge, in other words it does not attack the steel cleaning doctor by dissolving off small quantities of iron; and therefore the reds, pinks, and pale salmon and terra-cotta shades made with sulphocyanide of alumina as mordant are not dulled by admixture with dissolved iron salts, to which they are extremely sensitive. Iron dulls these delicate colours by forming a purple lake with the Alizarin.

The use of sulphocyanide of alumina is limited to the above purpose.

When heavy masses of dark red and light pink are printed in combination it is advisable to pass the goods through the rapid steam ager before subjecting them to the operation of steaming. If this is not done, the large quantity of acid liberated from the mordant fills the chamber and prevents the pinks from developing. The same effect is observable in other colours and with other mordants than sulphocyanide of alumina; in fact, it is always better to pass goods containing much acid through the rapid ager previous to steaming, since excess of acid in the steaming chamber naturally interferes with the decomposition of the mordants, and in many cases also destroys the colours, so that re-steaming is of no use.

Aluminium Citrate [$Al_2(C_6O_7H_5)_2$].—This mordant is used sparingly for the production of Alizarin pinks along with the above sulphocyanide of aluminium. It is prepared by dissolving aluminium hydrate in citric acid, and is usually kept on the acid side, as a little free acid affects the brightness of the pink beneficially.

ALUMINIUM CITRATE 40° Tw.

500 grms. 15½ per cent. aluminium hydrate paste.
220 ,, citric acid.
200 ,, water.

Stir until dissolved, and set at 40° Tw.

If too acid, add a little soda ash, say 25 to 30 grammes.

Aluminium Chlorate [$Al_2(ClO_3)_6$].—Aluminium chlorate finds a limited use in certain discharge styles. It is a powerful oxidising agent and must be used with care, otherwise the fibre is easily tendered. It is usually made by the double decomposition of aluminium sulphate and barium chlorate, but it may also be prepared by replacing the latter salt with potassium chlorate.

(1) ALUMINIUM CHLORATE 40° Tw.

I. { 40 kilos. aluminium sulphate.
30 ,, water.
II. { 60 ,, barium chlorate.
70 ,, water.

Mix. I. and II. together hot, stir well, allow to settle, and when cool, set at 40° Tw.

When potassium chlorate is used the following amounts are taken:—

(2) ALUMINIUM CHLORATE 40° Tw.

I. { 45 kilos. aluminium sulphate.
30 ,, boiling water.
II. { 49 ,, potassium chlorate.
100 ,, boiling water.

Mix the two solutions together hot, then allow to stand until the potassium sulphate crystallises out.

Chlorate of alumina is not often used alone at full strength, on account of its energetic action on the cloth. As a rule it is mixed with the milder chlorate of soda unless the colour to be discharged is very dark, and the pattern printed very lightly engraved, when chlorate of alumina and red prussiate of potash, with a little citrate of ammonia added, may be employed without fear of damage to the fabric.

Aluminate of Soda [$Na_2Al_2O_4$].—This mordant, more generally known as alkaline red mordant, is only employed in the printing of dyed styles. It is thickened with maize starch, printed, and after drying, the alumina is fixed

either by exposing the pieces to air from which they absorb carbonic acid, or by passing them through a solution of ammonium chloride, or a solution of a phosphoric acid made by decomposing commercial superphosphate with sulphuric acid.

Aluminate of soda is most readily prepared by dissolving dry aluminium hydrate in caustic soda. It may also be prepared directly from alum by adding strong caustic soda until the precipitate at first formed just re-dissolves. If potash is substituted for soda a purer mordant is obtained, as the sulphate of potash formed during the reaction crystallises out on standing. In the last case the mordant is, of course, aluminate of potash.

(1) Aluminate of Soda.

$\left\{\begin{array}{ll} 44 & \text{kilos. dry aluminium hydrate.} \\ 225 & \text{,, caustic soda 52° Tw.} \end{array}\right.$

Heat until the hydrate is dissolved; then cool and set at 36° Tw. The caustic soda is better added in two separate portions. Heat the first before putting in the aluminium hydrate; then add the second and heat the whole.

(2) Aluminate of Soda (from alum).

Precipitate 25 kilos. of alum with
107 ,, caustic soda 14° Tw.

Wash the precipitate well, filter it to a stiff paste, and then dissolve it in—
14 kilos. caustic soda 52° Tw.

Set at 36° Tw.

An excess of alkali is not detrimental to the mordanting properties of aluminate of soda, and it increases the stability of the solution.

The great drawback to the use of aluminate of soda as a general red mordant is that its nature prevents it being employed in combination with Aniline black, and other acid colours and mordants that are usually included in the madder style.

For plain red and pink prints, however, it is perfectly adapted, and can be used with conspicuous advantage in the printing of handkerchiefs which are required to be as good on one side as on the other. In fact, for all red and white styles it is a most useful and reliable mordant; it can be dried at a high temperature on steam-heated cylinders without any fear of the final colour being weak, as is the case with the acetates of alumina under similar conditions; and it is not possible for it to contain soluble iron salts, so that in this respect it is to be preferred to the acid mordants whenever circumstances allow of its employment.

Aluminium chloride has been suggested as a constituent of certain oxidation colours, and a chloride-acetate of alumina has been proposed as a suitable mordant for steam Alizarin reds. The latter may have yielded satisfactory results in the estimation of its inventor, but it certainly cannot compare with the other, and better known, mordants for Alizarin, and ought not to be regarded as even a moderate substitute for them.

(2) Iron Mordants.

In common with the aluminium mordants, the iron mordants have been in constant use from time immemorial; they are still amongst the most important substances employed by the dyer and calico printer, and are applicable to all textile fabrics.

Iron salts exist in two states of oxidation—the *ferrous* and the *ferric*—the corresponding salts of which are both used as mordants. The ferrous salts pass

into ferric salts by simple exposure to air, and are easily converted by oxidising agents, such as nitric acid, potassium chlorate, etc. As a rule, the ferrous salts are the most generally used by the calico printer, since it has been found by experience that the best results are obtained, in most cases, when the mordant exists on the fibre in a state intermediate between ferrous oxide (FeO) and ferric oxide (Fe_2O_3)—that is, as ferroso-ferric oxide (Fe_3O_4) or its hydrate [$Fe_3(OH)_8$]—and this state can be best attained by regulating the air-oxidation of ferrous salts. The ferric compounds find occasional application for the production of steam Logwood blacks on delaines and half-wool goods, but even here the ferrous compounds are quite as often used, and give on the whole a more pleasing shade of black. Ferric salts are also used for *dyeing* plain shades of Iron buff; but when the same shade is produced by *printing*, the ferrous salts are again the most generally preferred on practical grounds.

The following are the most important compounds of iron employed in calico printing:—

(1) **Ferrous Sulphate** [$FeSO_4.7H_2O$].—This salt, known as "copperas" and "green vitriol," forms the basis for the manufacture of most iron mordants, except the pyrolignite or "black liquor." It is manufactured on the large scale by dissolving scrap-iron in dilute sulphuric acid; or by the gentle oxidation of iron pyrites. By whichever process it is made it comes into the market in the form of light-green crystals, generally coated with an insoluble basic ferric sulphate, due to surface oxidation, if the crystals have been exposed to air for any length of time. A good quality of ferrous sulphate ought to be bright green, and free from contamination with copper or alumina.

Application to Cotton.—Copperas is rarely used as such for mordanting cotton in any way. It may be employed for the Iron buffs already mentioned, and is sometimes used for darkening basic colours dyed on a tannin mordant; but in general it oxidises too rapidly in solution to be of much value, except in cases where no better compound is available at the moment. It plays an important part as a reducing agent in Indigo dyeing, but otherwise its value in printing depends on its usefulness as the raw material for the preparation of other salts.

(2) **Ferrous Acetate** [$Fe(C_2H_3O_2)_2$].—For the printing of Iron buffs or Chamois this salt is invariably prepared by the double decomposition of ferrous sulphate and either acetate of lead or acetate of lime. The reaction is as follows:—

$$FeSO_4 + Pb(C_2H_3O_2)_2 = Fe(C_2H_3O_2)_2 + PbSO_4,$$

but, as in most mordants, molecular proportions are not strictly observed in practice, experience having shown that an excess of ferrous sulphate gives the best results. Prepared in this way ferrous acetate is really a mixture of the acetate and the sulphate, and is known as "buff mordant."

FERROUS ACETATE (BUFF MORDANT) 18° Tw.

68 kilos. of ferrous sulphate.
196 ,, ,, water.

Dissolve and add—

36 kilos. of acetate of lead.

Stir until all the lead acetate is dissolved, then settle, decant the clear liquor and set at 18° Tw. by the addition of water.

The above mordant, reduced in strength according to the shade desired, is thickened with starch or dextrin, printed and passed through the rapid steam ager. The goods are then raised through tepid caustic soda or sodium carbonate, and allowed to lie in the wet state until the more or less olive-

coloured precipitate of mixed ferrous and ferric oxides is wholly converted into the latter, which is the actual Iron buff colour.

By far the most important iron mordant, however, is the well-known "iron liquor," "black liquor," or pyrolignite of iron. This salt is prepared in immense quantities for calico printers by dissolving iron turnings and filings in pyroligneous acid (crude acetic acid). It is a dark-olive solution, standing at 24° Tw. In addition to ferrous acetate, it contains a notable quantity of organic matter consisting of tar and an iron salt of pyrocatechin, both of which retard its oxidation, and prevent its complete conversion into ferric oxide during the ageing process.

It is applied by printing in precisely the same way as the red liquors, and goes through an identical series of operations for its fixation, viz. ageing and dunging.

The ageing of black liquor printed for dyeing up in Alizarin requires to be conducted very carefully and not too rapidly, otherwise poor and uneven colours are the result. To avoid this, the goods are usually hung in an ageing room (where this exists), in preference to being passed through the rapid ager; the oxidation proceeds more slowly and regularly, and can be stopped at the right point. The rapid ager can, however, be used if the temperature is adjusted to the required degree; in fact, most goods are so treated nowadays, and with proper precautions the results leave nothing to be desired. Very weak iron mordants yield, however, very much better shades of purple with Alizarin if they are allowed to age slowly in a hanging room at a moderate temperature (70° dry-bulb, 66° wet-bulb thermometers). As already noted, the state of oxidation necessary is between ferrous and ferric oxide, consequently it is inadvisable to oxidise the goods rapidly by the ordinary methods of steaming, or of subjecting them to the action of oxidising agents like bichromate of soda, etc. In order further to retard the oxidation during ageing, it is a common practice to add a mild reducing agent in the form of sodium arsenite, which is dissolved either in water alone or in the iron liquor before it is thickened. Arsenious acid dissolved in glycerin, common salt, or ammonium chloride is also used for the same object, and is then known as "fixing-liquor." These additions are chiefly made to weak solutions of black liquor, such as are employed for the dyed lilac or purple style.

The effect of ageing is to drive off the greater part of the acetic acid, and at the same time to bring about the required degree of oxidation in the basic compound left on the fibre. Only practical experience can teach the printer or dyer to recognise the point at which the oxidation has proceeded sufficiently far.

After ageing, the printed goods are dunged in the usual manner, and afterwards dyed in Alizarin, Logwood, or any other colour that forms a lake with iron.

The most common use of pyrolignite of iron is for the production of black and white, or purple and white goods. At a strength represented by 8° Tw. it will yield a full deep black with either Logwood or Alizarin, and at strengths varying from 4° Tw. down to $\frac{1}{15}$° Tw. it gives a graduated range of purples, beginning with almost a black and going downwards to the most delicate tint of lilac. Simple black and white effects are mostly dyed with Logwood; black, purple and white combinations with Alizarin, since Logwood not only gives dirty greys on *weak* iron mordants, but is also a very fugitive colour to use for anything but dark shades of any description.

Pyrolignite of iron is not used for Iron buffs on account of the solid matter it contains—matter which frequently sticks on the cloth as black specks. Well filtered, it is used as a mordant in steam Alizarin purples, but these have lost

a good deal of their former importance since the introduction of mordant colours fixed with chromium salts. Occasionally it is employed as a fixing agent for tannic acid (with which it gives a blackish grey tannate of iron) in cases where a dark, dull shade is to be dyed with basic Aniline colours. For this purpose, however, the so-called nitrates of iron are generally preferred.

Ferrous Nitrate [$Fe(NO_3)_2$].
Ferrous Chloride ($FeCl_2$).
Ferrous Thiosulphate (FeS_2O_3).

These salts have not, so far, come into use as mordants proper. The first has been recommended as a buff mordant, and the last is said to yield good results when dried on the fibre; it decomposes, and on exposure to the air finally deposits a basic ferric sulphate on the cloth.

Ferrous nitrate made as follows is said to oxidise very slowly and to serve as an efficient mordant for Logwood blacks and Iron buffs.

Ferrous Nitrate—

I. { 1750 grms. ferrous sulphate.
2000 „ water.

II. { 2080 „ lead nitrate.
3000 „ water.

Mix the two solutions together; settle, and set the clear liquor at 50° Tw.

Trials made with the above against the ferrous acetate given previously did not compare favourably with the latter.

Potassium Ferrocyanide [$K_4Fe(CN)_6 + 3H_2O$].—*Yellow Prussiate of Potash.*—This salt occurs as light yellow crystals; it is used occasionally as a mordant for steam Alizarin purples, and as an oxygen carrier in Aniline blacks and certain oxidation discharges. Goods printed in Iron buff, when passed through an acidulated solution of potassium ferrocyanide, are dyed Prussian blue. For this purpose it was formerly used in large quantities, but Prussian blues are rarely dyed on cotton at the present time.

The sodium salt of ferrocyanic acid is rather cheaper and more soluble than the potassium salt, but it has the disadvantage of not forming so stable a mixture with Aniline when used as a constituent of Prussiate Aniline black.

Potassium Ferricyanide [$K_3Fe(CN)_6$].—*Red Prussiate of Potash.*—Potassium ferricyanide, like the preceding salt, is used as an oxygen carrier in both Aniline blacks and oxidation discharges. Printed on light, indigo-dyed cloth, it discharges the blue when passed through a hot solution of caustic soda.

Alkaline Iron Mordant.—Unlike aluminium hydrate, ferric hydrate is not soluble in excess of caustic soda or potash, but its precipitation may be prevented by the addition of suitable organic substances, and thus it can be obtained in alkaline solution. Of these substances, glucose, glycerin, and citric or tartaric acids are available; glycerin is perhaps the most effective from the point of view of the ultimate results.

Alkaline Iron Mordant.

{ 3 kilos. of ferric sulphate 91° Tw. (40 per cent. $Fe_2(SO_4)_3$).
$\frac{3}{4}$ „ glycerin.

14 „ caustic soda 70° Tw.

Cloth is padded and dried in the above and then exposed to the air, or simply padded and allowed to remain rolled up for some time, when the mordant decomposes depositing ferric oxide on the fibre; or after standing in batch for a short time the cloth may be passed through a solution of ammonium chloride 10° Tw. and fixed like the alkaline alumina mordant.

A somewhat different compound is obtained by using ferrous sulphate in place of the ferric salt; in other respects its action is similar.

Another alkaline iron mordant is prepared by dissolving the pyrophosphate of iron in ammonia. The ammonia is volatilised on drying, leaving the insoluble phosphate of iron on the fibre.

None of these alkaline mordants are used in practice, though they are said to give satisfactory colours when dyed up in Alizarin.

Ferric Sulphates.—Ferric salts are in general of little interest to the present-day calico printer. They are rarely used for steam colours, and only very occasionally for the fixation of tannic acid. By dyers, on the other hand, they are employed largely for black dyeing with Logwood—a branch of the industry outside the scope of this volume.

Under the general name of nitrate of iron, ferric sulphate is prepared by the oxidation of the ferrous salt in presence of free sulphuric acid,

$$6FeSO_4 + 3H_2SO_4 + 2HNO_3 = 3Fe_2(SO_4)_3 + 2NO + 4H_2O$$

and

$$12FeSO_4 + 3H_2SO_4 + 4HNO_3 = 3Fe_4(SO_4)_5(OH)_2 + 4NO + 2H_2O.$$

Basic salts may also be obtained by adding alkaline carbonates to the normal salt, but they dissociate on standing.

Ferric Sulphate, 90° Tw.

Mix together carefully:—

$$\left\{\begin{array}{l}\left\{\begin{array}{ll}15 \text{ kilos.} & \text{nitric acid } 66^\circ \text{ Tw.}\\ 20 \quad ,, & \text{water.}\end{array}\right.\\ \quad 7 \quad ,, \quad \text{sulphuric acid } 168^\circ \text{ Tw.}\end{array}\right.$$

Then add gradually—

40 kilos. ferrous sulphate (finely ground).

Heat to not above 50° C., and when the evolution of NO is finished add a further

3 kilos. nitric acid 66° Tw.

The above solution contains a little free nitric acid and sometimes about 2 per cent. of nitrous acid. If it be required neutral, add ferric oxide, not metallic iron, which would form a certain proportion of ferrous salt in all probability. At 90° Tw. this ferric sulphate contains 40 per cent. $Fe_2(SO_4)_3$.

Numerous other methods of manufacturing nitrate of iron are employed, but as none of the products are of present interest to calico printers it is needless to mention them.

The same remark applies to other ferric salts:—chloride, nitrate-acetate, nitrate-sulphate, acetate, sulphate-acetate, and a host of others sold under various trade names.

(3) Chromium Mordants.

The employment of chromium salts as mordants for cotton may be dated at the earliest from the introduction of Alizarin. One of these salts was certainly used as a mordant before this time, but it was considered rather as an oxidising agent than as a mordant, or as, in a sense, a colouring principle. Bichromate of potash, the salt in question, was employed for developing Catechu brown, for raising Chrome yellows, and for the mordanting of wool, but no other salt of chromium appears to have been used as a regular mordant until comparatively recent times. For one thing, no other salt was applicable to wool; and for another, the iron, aluminium, and tin mordants satisfied the needs of dyers and printers of the pre-Alizarin days.

At the present time chromium mordants are as important as the older aluminium and iron mordants—in fact, they are indispensable in many styles, since they form the fastest and most beautiful lakes with a great number of artificial dyestuffs.

The compounds of chromium exist in two states of oxidation: (1) chromic oxide (Cr_2O_3) and its salts; and (2) chromium trioxide (CrO_3) and the corresponding salts. In the first the chromium plays the part of the base, while in the second it forms the acid element of the salt. In both cases, however, the mordanting depends upon the deposition of chromic oxide (Cr_2O_3) or its hydrate [$Cr_2(OH)_6$] on the fibre, and therefore the salts corresponding to CrO_3—*e.g.* the chromates and bichromates—must be reduced to the lower state of oxidation (or the basic state) before they can be utilised as mordants. This reduction is effected either before they are applied to the fibre, or on the fibre itself, according to circumstances.

The most important salts of chromium used by the calico printer are the following:—chromium acetate, nitrate-acetate, sulphate-acetate, sulphocyanide, bisulphite, chlorate, chrome alum, the chromates and bichromates of soda and potash, and the alkaline chrome mordants. A brief description of the practical application of each of these will be given, beginning with the bichromates and chrome alum, both of which serve as the bases of most of the other chrome mordants.

Bichromate of Potash [$K_2Cr_2O_7$].—This salt comes into the market in the form of large triclinic orange-red crystals, containing no combined water. Its powerful oxidising property is utilised in the development of Catechu browns, Aniline blacks, Manganese bistres, and in the discharging of Indigo; and its power of precipitating lead salts is used in the production of the brilliantly coloured Chrome yellows and oranges. When treated in presence of sulphuric acid with reducing agents, *e.g.* sugar, starch, oxalic acid, sulphurous acid, glucose, alcohol, or glycerin, it is converted into a mixture of chromium sulphate and potassium sulphate (chrome alum), from which chromic hydrate can be precipitated by any alkali. On this account it is largely employed as the raw material for the preparation of other salts, either by double decomposition or by the solution of the hydrate in suitable acids.

The only application of bichromate of potash, as such, to the fibre for the object of mordanting, is by printing it along with magnesium acetate and sodium hyposulphite (thiosulphate). In the cold and away from strong light these salts have no action upon each other, but when printed on calico and then subjected to the action of steam the hyposulphite, in presence of magnesium acetate, decomposes and reduces the chromate to chromic sulphate, which reacts in turn with the magnesium oxide (left by the volatilisation of the acetic acid), with the result that chromic oxide is fixed upon the cloth. The following is one of several formulæ used in practice:—

Steam Chrome Mordant.

$\left\{\begin{array}{l}\text{16 kilos. bichromate of potash.}\\ \text{20 ,, boiling water.}\\ \text{15 ,, ammonia 20 per cent.}\end{array}\right.$

60 ,, thick starch paste or dextrin.
16 ,, thiosulphate of soda (finely ground).
15 ,, acetate of magnesium 14° Tw.

Print, dry, and steam for an hour. Then fix in a boiling 10 per cent. solution of sodium carbonate, wash, and dye in any suitable dyestuff. The final treatment in Na_2CO_3 (sodium carbonate) is to ensure that the chromium oxide

is fully fixed upon the fibre. If the cloth is to be mordanted throughout, it is passed in the open width through a padding mangle containing the above proportions of the various salts, but with the thickening replaced by water. The concentration of the bath may be varied as required.

In the discharging of Indigo a thickened solution of bichromate of potash (or chromate) is printed on the blue-dyed calico. After drying, and allowing to cool a little, the goods are passed through a tepid solution of sulphuric and oxalic acids (cutting liquor). Immediately they enter this cutting liquor the sulphuric acid liberates free chromic acid, and this at once oxidises and destroys the Indigo on the printed parts, thus producing a white pattern on a blue ground.

Potassium Chromate (K_2CrO_4) is a bright, lemon-yellow salt which crystallises in rhomboidal prisms. It is easily prepared by neutralising the bichromate with caustic potash, or potassium carbonate; the solution is concentrated to the crystallising point, or it may, if desired, be evaporated to dryness on a water bath, in which state it is usually employed for the making of coloured Indigo discharges.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Chromate of potash is preferred to the bichromate for mixing with albumen discharge colours for Indigo, because it contains no free acid. When the bichromate is used for this purpose, it is always neutralised by the addition of ammonia or sodium carbonate added to the printing paste, otherwise the albumen would be coagulated at once.

$$K_2Cr_2O_7 + 2(NH_4)OH = K_2CrO_4 + (NH_4)_2CrO_4 + H_2O.$$

The ammonium chromate acts in just the same way as the potassium salt when treated with sulphuric acid, namely, chromic acid is liberated and oxidises the Indigo wherever it is printed.

The chromates of lead and barium are insoluble salts. They are prepared by the double decomposition of soluble salts of either metal, and of chromate or bichromate of potassium. The lead salt is the well-known *Chrome-yellow*, and can be produced on the fibre by printing a thickened solution of lead acetate, and then running the goods through a solution of bichromate of potash.

Sodium Bichromate ($Na_2Cr_2O_7.2H_2O$) and sodium chromate ($Na_2CrO_4.10H_2O$) behave in all respects like the corresponding potassium salts. They are, however, more soluble, and are therefore to be preferred in all cases where concentrated solutions are to be printed. Bichromate of soda is rather hygroscopic, and requires to be kept in a dry place or in a closed-up cask; it is cheaper than bichromate of potash, and is capable of replacing it in all its applications, except in those where it is desirable that the sulphate produced in the manufacture of some chromium mordants should crystallise out. Potassium sulphate is much less soluble than sodium sulphate.

Chrome Alum [$K_2SO_4.Cr_2(SO_4)_3.24H_2O$].—An impure chrome alum, containing calcium sulphate and organic matter, is a by-product in the manufacture of Alizarin. It may be purified by re-crystallisation, and in this state it comes into the market as dark purple crystals isomorphous with potash alum. Although it contains no alumina its physical and chemical constitution is almost identical with that of the alums; hence its name *chrome alum*. A solution of chrome alum is frequently made in printworks by reducing bichromate of potash in presence of sulphuric acid. The following proportions may be used for this purpose:—

Chrome Alum Solution.

20 kilos. bichromate of potash.
50 „ water.
26·4 „ sulphuric acid 168° Tw.

Heat, and add gradually—

9 kilos. brown sugar.

Boil until the solution is of a bluish-green colour; if it is of an olive or yellowish-green colour it contains unreduced bichromate. Other substances, *e.g.* starch, glucose, glycerin, or the sulphites, may be used in place of sugar, with the same result. The preparation of chromium salts in this way is utilised in the manufacture of several mordants, the sulphuric acid being replaced by other acids.

Chrome alum dissolves in water to a violet solution, but if this solution be heated to 80° C. it turns green, and is said to contain a mixture of normal and basic salt. Practically speaking, it is immaterial which of these two solutions is used for the making of chrome mordants by double decomposition. They certainly act differently towards certain reagents—ammonia precipitates chromic hydrate from both solutions, but while that from the green solution is insoluble in excess of ammonia, the reverse is the case with that from the violet—and they yield corresponding acetates which form basic salts of different degrees of stability; but as none of these basic salts are used in calico printing, and as the normal salts employed are all sufficiently stable, it is unnecessary to draw a distinction between them here.

Basic chromium sulphates are prepared by adding calculated amounts of chromium hydroxide or of alkaline carbonates to the normal salt. They, of course, contain sodium or potassium sulphates, but these do not appear to affect their dissociation point on heating. The basic sulphates deposit a larger quantity of chromic oxide on the fibre as their basicity increases.

Pure chromium sulphate may be obtained by dissolving the hydrate in sulphuric acid. It has no advantages over commercial chrome alum for the preparation of mordants, and is of no practical interest, as it is not an article of commerce, and requires to be prepared specially if wanted in any quantity for a particular purpose.

Chromium Acetate [$Cr_2(C_2H_3O_2)_6$].—This salt is the most important of the chromium mordants. Its stability is such that it can be boiled and diluted to any extent without dissociating, and yet it combines easily with various colouring matters to form lakes remarkable for their beauty and fastness.

Acetate of chrome is prepared on the large scale in three different ways—*e.g.* (1) by dissolving chromium hydrate in acetic acid; (2) by the double decomposition of chrome alum and lead acetate; and (3) by reducing bichromate of potash or soda in the presence of acetic acid. The following formulæ illustrate the practical application of these three methods. In each case the solution contains a little free acid, which is found beneficial in most instances.

Acetates of Chrome.

$$\text{I.}\begin{cases}\text{1200 grms. of chromium hydrate 20 per cent. paste.}\\ \text{1500 ,, acetic acid 9° Tw.}\end{cases}$$

Heat till dissolved, cool, and set at 25° Tw.

$$\text{II. } a\begin{cases}\text{1200 grms. chrome alum.}\\ \text{2500 ,, water.}\end{cases}$$
$$b\begin{cases}\text{1350 ,, lead acetate.}\\ \text{1000 ,, water (or acetic acid at 2° Tw.).}\end{cases}$$

Mix *a* and *b* together, settle, decant the clear liquor, and set at 25°–32° Tw.

This solution contains potassium sulphate; if 1800 grms. of lead acetate were used it would contain potassium acetate, which promotes the solution of lead sulphate—a circumstance to be avoided.

III. { 12 kilos. of potassium bichromate.
15 „ water.
30 „ acetic acid 9° Tw.

Heat to 180° F. and then add gradually 7 kilos. glucose.

When the reaction has finished, heat the whole until it becomes green. Then set at 25°-32° Tw.

Basic acetates are prepared either by the double decomposition of basic chromium sulphate and lead acetate or by adding alkaline carbonates to the normal acetate. They are very rarely used, and then only in cases where the colour is dissolved in weak alkalies. What is known as neutral acetate is much more commonly employed.

NEUTRAL ACETATE OF CHROME.

{ 1200 grms. chromium hydrate 20 per cent. paste.
1300 „ acetic acid 9° Tw.
200 „ glycerin.

Heat till dissolved, and add about 80 grms. of 10 per cent. solution soda ash (or until the acetate ceases to show an acid reaction).

It is possible that basic acetates might be used with advantage in many styles of work, but they have never been applied to any extent on the large scale. An acetate made according to the following equation is very stable :—

$$Cr_2(SO_4)_2(OH)_2 + 2Pb(C_2H_3O_2)_2 = Cr_2(OH)_2(C_2H_3O_2)_4 + 2PbSO_4.$$

It will stand a fair amount of heating, and does not begin to dissociate until it is diluted with seventy-five times its own volume of water or starch paste, and then only on heating. When printed and sharply dried it yields something more than 25 per cent. of its available chromic oxide to the fibre, and when steamed and fixed in boiling sodium carbonate it gives up almost the whole. Hence it ought to be a useful mordant for the production of two-colour effects on chrome mordanted cloth which is afterwards dyed.

Nitrate-Acetate of Chrome [$Cr_2(NO_3)_2(C_2H_3O_2)_4$].—The nitrate-acetates of chromium are only used in calico printing for such colours as are improved by a slight oxidation—*e.g.* Logwood black, Quercitron bark, Persian berry yellows in strong shades, and Peachwood.

They are most easily prepared by double decomposition thus :—

$$K_2Cr_2(SO_4)_4+Pb(NO_3)_2+2Pb(C_2H_3O_2)_2=Cr_2(NO_3)_2(C_2H_3O_2)_4 + 3PbSO_4 + K_2SO_4$$

NITRATE-ACETATE OF CHROME.

a { 1000 grms. chrome alum.
2000 „ water.

b { 300 „ lead nitrate.
770 „ lead acetate.
1500 „ water.

Mix *a* and *b* together, settle, and set the clear liquor at 35° Tw.

A basic nitrate-acetate of chrome is the compound most generally used whenever a nitrate-acetate is required. It may be prepared by adding sodium

carbonate to the foregoing normal salt, but the most convenient method to adopt is to make it from bichromate by reduction with glucose.

$$2K_2Cr_2O_7 + 6HNO_3 + 4C_2H_4O_2 + 6H_2 = 2Cr_2(NO_3)(C_2H_3O_2)_2(OH)_3 + 4KNO_3 + 8H_2O.$$

Basic Nitrate-Acetate of Chrome.

$\left\{\begin{array}{l}\text{3000 grms. potassium bichromate.}\\ \text{3000 ,, boiling water.}\\ \text{3600 ,, nitric acid 64° Tw.}\end{array}\right.$

Add carefully, stirring all the time, 900 grms. glucose 33 per cent. (or glycerin), and then 5000 grms. acetic acid 9° Tw.

Allow the solution to stand until the potassium nitrate has crystallised out; then reduce to 40° Tw. with acetic acid at 4° Tw.

The glucose in the above formula may be replaced by 900 grammes of glycerin, which must be added with the greatest care, and in small quantities at a time.

Chromium Sulphate-Acetates $[Cr_2(SO_4)(C_2H_3O_2)_4]$.—These salts are made by incompletely precipitating the sulphuric acid in chrome alum or chromium sulphate.

$$K_2Cr_2(SO_4)_4 + 2Pb(C_2H_3O_2)_2 = Cr_2(SO_4)(C_2H_3O_2)_4 + K_2SO_4 + 2PbSO_4.$$

They may also be prepared by a method analogous to that employed in the manufacture of the nitrate-acetates of chrome, viz. by the reduction of the bichromates of potash or soda in presence of the necessary acids.

I. Sulphate-Acetate of Chrome 40° Tw.

$\left\{\begin{array}{l}\text{3000 grms. chrome alum.}\\ \text{6000 ,, water (boiling).}\end{array}\right.$
$\left\{\begin{array}{l}\text{2250 ,, acetate of lead.}\\ \text{1200 ,, boiling water.}\end{array}\right.$

Add the two hot solutions together; allow to settle and cool, and set at 40° Tw.

II. Sulphate-Acetate of Chrome 40° Tw.

18,000 grms. bichromate of potash.
15,000 ,, sulphuric acid 168° Tw.
60,000 ,, hot water.
9,000 ,, acetic acid 9° Tw.

Add gradually—

9,000 ,, brown sugar and then
9,000 ,, acetic acid 9° Tw.

Heat until the solution turns green. If it persistently retains an olive colour, the bichromate is incompletely reduced, and more sugar, or whatever reducing agent has been used, must be added.

Although the sulphate-acetates of chrome are largely used in place of the normal acetates, it is questionable whether they are equally effective. Comparative trials seem to show that they are not, for of several colours made up with both mordants, those containing the normal acetate invariably gave the darkest shades. On repeating the experiments with the addition of acetate of lime to the colours containing the sulphate-acetate, both sets of colours gave practically identical shades on steaming and washing; so that it would appear that the best results are only obtainable when the sulphuric acid is completely replaced by acetic acid. The only effect of adding acetate of lime to the sulphate-acetate colours was to do this, since the same addition to the acetate

colours did not influence them in the least, except in the case of those containing Alizarin, and then both series of trials yielded the same shades.

In many instances, too, the sulphate-acetates of chrome coagulate and render insoluble the gum Senegal thickening used in blotch colours for the express purpose of keeping the cloth soft. This sometimes occurs with pure acetate of chromium made from the hydrate, but much less frequently than with the sulphate-acetates, hence it is safer to use the pure salt in all cases where any uncertainty exists as to the behaviour of the gum during the steaming process.

Chromium Sulphocyanide [$Cr_2(CNS)_6$].—This mordant is of only occasional use—chiefly for pale shades of "crushed strawberry" and such colours as are sullied by traces of iron dissolved off the steel cleaning doctor by slightly acid mordants. It is prepared in two ways: (1) by mixing solutions of chrome alum and barium sulphocyanide; and (2) by replacing the latter salt with calcium sulphocyanide. The first is the method generally adopted in practice.

$$K_2Cr_2(SO_4)_4.24H_2O + 3Ba(CNS)_2.2H_2O = Cr_2(CNS)_6 + K_2SO_4 + 3BaSO_4 + 26H_2O.$$

CHROMIUM SULPHOCYANIDE.

$\left\{\begin{array}{l}\text{3000 grms. chrome alum.}\\ \text{6000 ,, boiling water.}\end{array}\right.$

Add—

2580 ,, barium sulphocyanide (crystals).

Stir until dissolved, allow the precipitate of barium sulphate to settle, and then decant the clear solution. Let the potassium sulphate crystallise out as much as possible, and then set the solution at 32° Tw.

Chromium sulphocyanide is also used as a mordant in the printing of steam Logwood blacks, though the acetates answer quite as well.

Chromium Chlorate [$Cr_2(ClO_3)_6$].—Chromium chlorate is a powerful oxidising agent; it smells strongly of chlorine, and when heated gives off copious fumes of the oxides of chlorine. It has been recommended by Prud'homme for the production of ungreenable Aniline blacks, and has been occasionally used in small quantities as an addition to Logwood blacks. Its employment is somewhat dangerous in any case, since the fibre is exceedingly apt to become tendered by the formation of oxycellulose. According to Lauber, basic chlorate of chrome serves admirably as a mordant for Catechu browns, and this is quite likely, considering the energetic oxidising action of the chlorates in general.

Chlorate of chrome is prepared by the double decomposition of chrome alum and barium chlorate, or by mixing hot solutions of chrome alum and potassium chlorate.

I. CHLORATE OF CHROME.

$a\left\{\begin{array}{l}\text{3000 grms. chrome alum.}\\ \text{6000 ,, boiling water.}\end{array}\right.$

$b\left\{\begin{array}{l}\text{2890 ,, barium chlorate.}\\ \text{2250 ,, boiling water.}\end{array}\right.$

Mix together, and after settling, reduce to 20° Tw.

II. CHLORATE OF CHROME.

$a\left\{\begin{array}{l}\text{3000 grms. chrome alum.}\\ \text{6000 ,, boiling water.}\end{array}\right.$

$b\left\{\begin{array}{l}\text{2200 ,, potassium chlorate.}\\ \text{4500 ,, boiling water.}\end{array}\right.$

Mix together, cool, and allow the potassium sulphate to crystallise out. Then set at 20° Tw.

Chromium Bisulphite.—This mordant is of uncertain composition. It may be obtained by mixing bisulphite of soda with chrome alum or chromium sulphate solutions. When padded on calico and steamed, it yields a large amount of its available chromium to the fibre in the form of hydroxide, and a further amount can be fixed by a treatment in hot soda. It is chiefly used for the production of the chrome mordant dyed and discharged style, and is also employed as a mordant for certain steam colours—*e.g.* Alizarin greens and Alkaline and Alizarin blues.

Alkaline Chrome Mordants.—These mordants are not used for printing, but only for mordanting cloth that is intended for the dyed and discharged style. For this purpose the goods are first padded in the open width in an alkaline solution of chromium hydrate, then fixed, dried, and again printed with an acid discharge, which dissolves out locally the chromium hydrate, so that on subsequently dyeing, a white pattern on a coloured ground is obtained. If sodium phosphate (Na_2HPO_4) be printed instead of an acid, a half-discharge effect is the result. The phosphate of chrome has less attraction for the colouring matter than the hydrate or oxide; hence, in those parts where the phosphate of soda was printed, the cloth dyes up a lighter shade.

One of the first and most successful alkaline chrome mordants is that worked out by H. Koechlin. He observed that cotton is capable of absorbing chromium hydrate from alkaline solutions, or at least of becoming mordanted when impregnated with such solutions. The more alkaline the solution, the greater is the quantity of chromium hydrate deposited on the fibre. Koechlin's process, as worked on the large scale by one of the most important English firms, is as follows:—

The cloth is padded in an alkaline mordant as under:

Alkaline Chrome Mordant.

20 kilos. chrome alum.
100 ,, water.
60 ,, caustic soda 70° Tw.

After padding, the goods are batched and allowed to lie all night; or they are simply plaited down and left exposed to the air for twelve to fifteen hours. At the end of this time most of the chromium hydrate will be fixed on the fibre. The goods are then well washed in water, and after drying are ready for printing.

This alkaline mordant does not keep well; on standing a day or two precipitation takes place. The addition of glycerin tends to lessen this liability, but it also diminishes the mordanting power of the solution. The precipitation is hastened by the presence of the sulphates of soda and potash, and it was the recognition of this fact that led H. Schmid to suggest the preparation of alkaline chrome mordants from the hydrate. Made on these lines the mordant is manufactured as follows:—

Alkaline Chrome Mordant.

$\begin{cases} \text{3,000 grms. chrome alum.} \\ \text{15,000 ,, boiling water.} \end{cases}$

Cool and precipitate the hydrate with—

$\begin{cases} \text{1,000 grms. soda-ash.} \\ \text{5,000 ,, water.} \end{cases}$

Wash and filter the precipitate and then dissolve it in

150 grms. caustic soda at 50° Tw.

The treatment of the cloth is identical with that in Koechlin's process.

Another alkaline mordant is based upon the fact that bichromate of potash and bisulphite of soda have no action upon each other in the presence of ammonia. On steaming, however, the ammonia is volatilised, and the bichromate is reduced with the precipitation of chromium hydrate on the fibre. In practice this process is worked with the following materials and proportions:—

ALKALINE CHROME MORDANT.

$\left\{\begin{array}{l}\text{10 kilos. bichromate of potash.}\\ \text{100 ,, water.}\end{array}\right.$

Dissolve, cool, and add—

20 kilos. ammonia 20 per cent.
30 ,, bisulphite of soda, 56° Tw.

Make up with water to 200 litres.

The cloth is padded in this solution, dried and passed through the rapid ager, and then washed.

A mordant somewhat similar to the last has been used with excellent results for the discharged and half-discharged chrome mordant style. It is prepared as follows:—

ALKALINE MORDANT.

200	grms.	bichromate of soda.
200	,,	acetate of soda.
300	,,	ammonia.
210	,,	hydrosulphite-formaldehyde (Formosul).
4000	,,	water.

Pad the cloth in this solution, dry in hot air, pass through the rapid ager, and then through a boiling 2 per cent. solution of sodium carbonate, wash and dry. This mordant printed with citric acid and di-sodium phosphate gives good white and half-discharge effects when dyed up in Alizarin, Cœrulëin, Nitro-alizarin, etc. The fixing in sodium carbonate is not absolutely essential, but it ensures the complete fixation of the chromic hydrate, and, as far as experience goes, yields better results. Rather better discharges are obtained if the padded and dried cloth is printed before ageing, the citric acid itself reducing the bichromate, with the formation of a very soluble citrate.

All the alkaline chrome mordants are prone to decompose on standing, and should therefore only be prepared as they are required.

Chromate of Chromium.—The mordants formerly sent out by Meister, Lucius & Brüning, under the names of Chrome Mordants Ga I, Ga II, Ga III, consist of various basic chromates of chromium, containing a little acetic or hydrochloric acid. The acetic acid compound is the one most generally employed for cotton. Under the influence of steam it is completely reduced, and is then fixed in soda. For dark dyed shades the following formula is recommended by the makers:—

CHROME MORDANT Ga II.—

200	c.c.	chrome mordant Ga II, 64° Tw.
30	,,	glycerin.
770	,,	water.
1000		

Pad the cloth in this solution, dry it in a hot-air machine, pass it through the rapid ager, and then fix the mordant by passing the cloth in the open width through a 3 per cent. solution of soda-ash at 80° C. After washing and

drying, it is ready for printing in citric acid, or, if intended for a plain shade, for dyeing at once.

The chromate of chromium mordants are prepared by dissolving the hydroxide in chromic acid, and then adding suitable quantities of acetic and hydrochloric acids according to circumstances. In using them care must be taken to keep the padded cloth away from the light until after it is steamed, otherwise the chromic acid will oxidise and tender the fibre.

Tartrates and Citrates of Chrome.—These two salts are not capable of mordanting cloth, but as they are largely used as resists under steam Alizarin reds and pinks, mention of them will be as convenient here as elsewhere. They possess the advantage of giving a perfectly white resist which does not run in steaming, like the citrates of soda, and citric and tartaric acids, which are used for the same purpose.

CITRATE OF CHROME 42° Tw. (For pink resists.)

$\left\{\begin{array}{ll} 125 \text{ grms.} & \text{bichromate of potash.} \\ 525 \quad ,, & \text{hot water.} \end{array}\right.$

Add gradually—

350 ,, powdered citric acid.

Cool, and set at 42° Tw. by adding water.

ACID TARTRATE OF CHROME 78° Tw. (For dark red resists.)

$\left\{\begin{array}{ll} 585 \text{ grms.} & \text{bichromate of soda.} \\ 2000 \quad ,, & \text{water.} \end{array}\right.$

880 ,, powdered tartaric acid.

Set at 78° Tw.

The application of these salts will be given when treating of resists and discharges.

(4) Tin Mordants.

Various tin salts play an important part in many styles of printing. They act as mordants, brightening agents, and discharging agents, and are altogether an indispensable series of bodies to the calico printer.

Tin occurs in two states of oxidation: stannous oxide (SnO) and stannic oxide (SnO_2). Both these bodies are soluble in acids and alkalies, thus forming four distinct classes of salts, namely, the stannous and stannic salts, in which the tin acts as the base; and the stannites and stannates, in which it acts as the acid. The stannous salts are powerful reducing agents: they have a great affinity for oxygen, and if exposed to air for long they are more or less converted into the extremely stable stannic salts. In practice this property is taken advantage of in the discharging of direct-dyeing colours. Iron buffs, Manganese browns, etc., and in resisting Azoic colours.

Of the acid salts (that is, those in which the base is tin), both classes are used largely; but of the others, only stannate of soda is used to any extent, although the stannite is sometimes employed in the discharging of Turkey-red, and a few special discharge effects on the direct colours.

Stannous Chloride ($SnCl_2.2H_2O$).—This salt is made by dissolving granulated tin in hydrochloric acid. It comes into the market in the form of moist-looking crystals, and is commonly known as "tin salt" and "tin crystals." If dissolved in a very small quantity of water a clear solution is obtained, but on adding more water the solution becomes milky, owing to oxidation and

simultaneous precipitation of some oxychloride. Stannic chloride is formed at the same time.

$$3SnCl_2 + O + H_2O = 2Sn(OH)Cl + SnCl_4.$$

The oxychloride re-dissolves on the addition of a little hydrochloric acid. A similar oxidation product is formed on the surface of tin crystals if they be exposed for any length of time to the combined action of light, air, and moisture.

APPLICATION.—Mixed in small quantities with thickened red liquors, tin crystals serve to prevent the fixation of iron on the cloth during the ageing process, and thus ensure the brightness of the Alizarin red subsequently dyed upon the cloth. When added to the extent of from 3 per cent. to 5 per cent. they enable the red mordant to resist purple covers and pads (weak iron mordants) printed over it, and so make it possible to produce a bright red object on a plain or figured purple ground.

The energetic reducing action of tin crystals is utilised in the discharging of many colours, though its importance in this respect has diminished since the introduction of hydrosulphites. It is still, however, employed almost exclusively for resisting the fixation of the insoluble azo colours on β-naphthol prepared cloth, and for this purpose it is so far unsurpassed. (See also Oxidising and Reducing Agents.)

As a mordant, tin crystals, in conjunction with acetate of soda, finds an occasional application in the printing of Persian berries, with which it forms an exceedingly brilliant reddish-yellow lake, fast to light and soap. Its use as a mordant for steam colours is attended by some risk of tendering the fibre, notwithstanding the presence of acetate of soda, and consequently it is generally replaced by other stannous salts, and sometimes by the hydrate, especially when a mixed aluminium and tin mordant is required, as in the case of a particularly brilliant steam Persian berry yellow.

Apart from its employment as a discharging and reducing agent stannous chloride serves as the chief point of departure for the preparation of other tin mordants, and this, at the present time, perhaps, is its most important use in the calico-printing industry.

Stannous Acetate [$Sn(C_2H_3O_2)_2$].—This salt is still largely used in the production of discharge effects on grounds dyed with the Benzidine, Diamine, and other series of direct dyeing colours, and, to a slight extent, as a mordant for the vegetable colouring matters.

It is most conveniently prepared by the double decomposition of stannous chloride and lead acetate.

STANNOUS ACETATE (Acetate of Tin) 30° Tw.

a	1390	grms.	lead acetate.
	800	,,	water.
	300	,,	acetic acid 9° Tw.
b	1125	,,	stannous chloride.
	300	,,	water.
	600	,,	acetic acid 9° Tw.

Mix *a* and *b*, allow the lead chloride to settle, and then set the clear solution at 30° Tw.

Prepared in this way the solution of tin acetate ought to be quite clear. It contains free acetic acid, but this is no detriment, especially when it is used for discharge colours containing tannic acid; moreover, it prevents the precipitation of basic salts, which are apt to stick in the engraving during printing.

Stannous Nitrate [$Sn(NO_3)_2$] (?).—The composition of nitrate of tin is uncertain. It is made by slowly dissolving rods of tin in cold dilute nitric acid

free from the lower oxides of nitrogen. Great care should be taken to regulate the reaction so as to avoid the evolution of NO_2.

Nitrate of Tin 54° Tw.

5 kilos. of tin rods or small blocks.
40 ,, nitric acid 30° Tw.

Allow the reaction to proceed slowly until the acid is saturated. Then set at 54° Tw. by adding water.

On standing for a lengthened period, stannous nitrate deposits a white insoluble body—probably meta-stannic acid.

Nitrate of tin, formerly used as an assistant mordant in steam Alizarin reds, is now practically obsolete, except in the wool dyeing trade for the production of Cochineal scarlets, etc.

Citrate of Tin.—A mordant under this name is frequently used in combination with acetate of chrome for the production of a quiet lemon yellow from Persian berries extract. As used, it is not a solution, but merely a kind of pasty precipitate, which dissolves when added to the printing colour; probably it exists partly in solution and partly in a salted out state, as might be expected from the mode of its preparation.

Citrate of Tin.

{ 48 kilos. citric acid.
{ 90 ,, water.

Dissolve, cool, and add—

21·5 kilos. crystal carbonate of soda.

and then—

33 ,, stannous chloride.

Stir till the mixture thickens, and stir up every time before use.

Oxalate of Tin [$Sn(C_2O_4)_2$].—Oxalate of tin is one of the most important ingredients in steam Alizarin red, towards which it acts both as a true mordant and as a brightening agent. Without the presence of tin salts it is impossible to obtain a brilliant red in the steam style, and the oxalate is the best to use for this purpose. As generally made, oxalate of tin is a mixture of the stannous and stannic salts, since it is prepared from oxymuriate of tin, itself a mixture of nitric acid with tin crystals. On the large scale the following method is adopted for its manufacture:—

Oxalate of Tin.

{ 10 kilos. oxymuriate of tin.
{ 40 ,, water.

Precipitate the above with—

{ 3 kilos. soda-ash.
{ 20 ,, water.

Settle, run off the supernatant liquor, wash the precipitate three times by decantation, and then filter and press it to a stiff paste (about 15 kilos. in weight). Finally, add to it 1400 grammes of oxalic acid, dissolved in sufficient water to make the whole up to 20 kilogrammes, and heat until the whole is thoroughly homogeneous. The heating is carried out in a deep earthenware pot or mug, placed in boiling water in a colour pan. By substituting 1200 grms. of tartaric acid for oxalic acid the corresponding tartrate of tin may be obtained.

Stannic oxalate is made in the same way, except that stannic chloride is used in place of the oxymuriate.

I. Stannic Oxalate.

$\left\{\begin{array}{l}\text{5 kilos. stannous chloride} \\ \text{5 ,, hydrochloric acid 24° Tw.}\end{array}\right.$ $\left.\begin{array}{l} \\ \\ \text{0·8 ,, chlorate of soda}\end{array}\right\}$ Stannic chloride.

The chlorate of soda must be added as rapidly as the reaction permits, and the solution of tin salt in hydrochloric acid must be gently heated at first in order to promote the beginning of the reaction. When the latter is finished the solution is diluted with 20–30 kilos. of water, and the stannic hydrate precipitated with about 3 kilos. of soda ash dissolved in 30 kilos. of water. Wash and filter the precipitate as above, and then dissolve it in 1400 grammes of oxalic acid and sufficient water to make the whole up to 20 kilogrammes.

Another *stannic oxalate* used for preparing an oil mordant is made by adding a solution of oxalic acid to a solution of stannous chloride in nitric acid, or by adding stannous chloride slowly to a mixture of nitric and oxalic acids. The former is the most rational method, but the latter is almost invariably adopted in practice, and gives satisfactory results, so far as can be judged from the quality of the work produced.

II. Stannic Oxalate.

2 kilos. nitric acid 57° Tw.
1 ,, warm water.
1½ ,, oxalic acid.

Add gradually—

6¼ kilos. stannous chloride.

In this case the stannic oxalate is in solution, and mixed with hydrochloric acid. Probably the same compound would result from using a mixture of tin oxymuriate and oxalic acid, though what actually takes place during these reactions is not easy to explain.

Oxymuriate of Tin.—This product is simply a mixture of nitric acid and tin crystals, and varies a good deal in composition.

Oxymuriate of Tin.

30 kilos. of nitric acid 57° Tw.

Add gradually—

$\left\{\begin{array}{l}\text{50 ,, stannous chloride.} \\ \text{20 ,, water.}\end{array}\right.$

100

Oxymuriate of tin is thus made in practice. It is only used for the preparation of other mordants in calico printing; it varies considerably both as regards its percentage of tin and its acidity; and unless made on the spot, it is impossible to say exactly in what state of oxidation the tin really exists; in fact it is at all times difficult to ascertain the true composition of an oxymuriate of tin.

Stannate of Soda (Na_2SnO_3).—In this salt the stannic oxide acts as the acid; and as it is precipitated by dilute mineral acids it is easily applied to the fibre. Stannate of soda is prepared by fusing together metallic tin, caustic soda, and sodium nitrate, and sometimes common salt.

$$2Sn + 3NaOH + NaNO_3 = 2Na_2SnO_3 + NH_3.$$

The melt is broken up and sent into the market as white, fused-looking lumps, which, when fresh, are entirely soluble in water, but undergo decomposition when exposed to moist air and become partially insoluble.

APPLICATION.—The chief use of stannate of soda is for the preparation of cloth for printing. The cloth is padded in a solution of stannate at about 6° Tw.; squeezed and passed without drying (though it may be dried) into sulphuric acid at 3°–4° Tw.; well washed and dried.

$$SnO_3Na_2 + H_2SO_4 + H_2O = Sn(OH)_4 + Na_2SO_4.$$

The presence of stannic oxide on the cloth enhances the brightness of the printed colours, and increases their fastness to washing. Formerly stannate of soda was largely employed for the preparing of goods for the steam style, but it is now usually replaced by oleine or sulphated oil. It is still used for making eosine lakes.

Stannite of Soda (Na_2SnO_2), prepared by dissolving stannous hydrate in caustic soda, is only used in some methods of Turkey-red discharging.

A few other compounds of tin, only employed occasionally for special styles, are readily replaceable by the mordants already given, and therefore do not call for particular mention.

(5) Nickel Mordants.

The only nickel salts in general use are the sulphate, the acetate, and the bisulphite.

Nickel Sulphate ($NiSO_4.7H_2O$) is a green-coloured salt, easily soluble in water. It comes into the market in crystals, and its sole use is for the preparation of the acetate.

Nickel Acetate [$Ni(C_2H_3O_2)_2$] is prepared by the double decomposition of nickel sulphate and lead acetate.

$$NiSO_4 + Pb(C_2H_3O_2)_2 = Ni(C_2H_3O_2)_2 + PbSO_4.$$

NICKEL ACETATE.

a { 28 kilos. nickel sulphate.
  50 ,, water.
b { 38 ,, $Pb(C_2H_3O_2)_2$ lead acetate.
  20 ,, boiling water.

Mix *a* and *b* together hot, allow to settle and cool, and set at 20° Tw.

The chief use of nickel acetate is as a mordant for Alizarin blue.

Nickel Bisulphite comes into commerce as a green solution marking 32° Tw. It is often employed instead of the acetate for the printing of Alizarin blue, and also in combination with acetate of chrome for Alizarin green S. and similar bisulphite compounds of the mordant colouring matters.

(6) Zinc Mordants.

The zinc compounds play a not unimportant part in the production of many styles of printing.

Only the acetate and bisulphite are employed as mordants proper, and then they are restricted to the fixation of Alizarin blue, with which they form a very beautiful lake, much purer than that obtained with chrome mordants. Zinc oxide is the basis of several processes for the resisting of prussiate Aniline black (the well-known Prud'homme style), and it not only prevents the development of the black, but also forms simultaneously ferrocyanide of zinc, which acts as a mordant for any basic colours with which it may be mixed.

The following are the most important zinc salts and compounds used in calico printing:—

Zinc Sulphate ($ZnSO_4.7H_2O$).—This salt is employed, like the acetate, for the fixation of Alizarin blue. It is prepared by dissolving zinc in sulphuric acid, and as a commercial product it comes into the market as white crystals, known commonly as " white vitriol." Its chief use is for the preparation of other zinc mordants.

Zinc Bisulphite [$Zn(HSO_3)_2$].—A very rarely used mordant for Alizarin blue, and of very little practical interest. It is sold as a yellowish fluid standing at 30° Tw. Zinc bisulphite is capable of giving good results with Alizarin blue, but on the whole it is a quite unnecessary mordant, since it can be replaced with advantage by either the acetate or the cheap sulphate.

Zinc Acetate [$Zn(C_2H_3O_2)_2$].—Zinc acetate is made by mixing solutions of zinc sulphate and lead acetate.

$$ZnSO_4 + Pb(C_2H_3O_2)_2 = Zn(C_2H_3O_2)_2 + PbSO_4.$$

Acetate of Zinc 30° Tw.

3000 grms. zinc sulphate.
5000 ,, boiling water.

Stir in, until dissolved—

4000 grms. lead acetate.

Settle, cool, and set the clear liquor at 30° Tw.

Zinc acetate serves both as a mordant for Alizarin blue and as a resist for Aniline black in cases where the presence of solid substances like zinc oxide, chalk, magnesium, carbonate, etc., is objectionable—*e.g.* in many flannelette styles. Used in place of acetate of soda for neutralising diazo solutions, it allows of these colours (the insoluble azo colours) being employed under Aniline black covers (Plusanski's process). It also acts, in common with sulphate of zinc, as a resist to pigment colours, and it is largely used for this purpose when thickened with dextrin and mixed with china clay.

Zinc Chromate ($ZnCrO_4$).—Zinc chromate finds an occasional use in the production of the indigo reserve style. It is a pale yellow precipitate, obtained by mixing solutions of zinc sulphate and potassium bichromate or chromate.

Zinc Chromate.

$$a\begin{cases}4 \text{ kilos. of potassium chromate.}\\ 5 \quad ,, \quad \text{water.}\end{cases} \qquad b\begin{cases}3 \text{ kilos. of zinc sulphate.}\\ 5 \quad ,, \quad \text{water.}\end{cases}$$

Mix *a* and *b* hot, allow to settle; then wash the zinc chromate by decantation several times and filter it down to 3600 grammes=50 per cent. paste.

Zinc chromate mixed with a suitable resist paste printed on *light indigo dyed cloth* constitutes a resist discharge; and if associated in a two-colour pattern with a simple indigo resist paste gives rise to the *two blue and white* indigo reserve style. After printing, the light blue cloth is passed again through the indigo vats; the Indigo only dyes the unprinted portions, and when the cloth is subsequently treated in a bath of sulphuric and oxalic acids, chromic acid is liberated from the zinc chromate and discharges the light blue over which it was originally printed. On washing, the other reserve is removed; and as it contained no chromate, it simply leaves a light blue where it was printed, thus giving an effect of white and light blue on a dark blue ground.

Zinc Oxide (ZnO).—Zinc oxide is one of the most useful resisting agents for prussiate or other Aniline blacks; and as it is easy to work, keeps well in made-up colours, yields very bright coloured discharges, and has no injurious effect on either colours or cloth, it is now generally employed in all Prud'homme

styles where solid matter in the material is of no moment. It is also used for the production of imitation damask effects, for which purpose it is mixed with a little albumen and a gum tragacanth thickening, and printed either as white on white cloth or slightly tinted with any suitable colouring matter. On mercerised sateen the contrast between the dull matt surface of the zinc oxide and the silky lustre of the cloth gives a very pleasing damask effect.

In making printing pastes from zinc oxide, care must be taken to grind it to the finest state of division possible, and to strain it thoroughly before printing, otherwise sticking-in and scratched rollers may be expected.

Zinc oxide, being an exceedingly white substance, and having a good covering power, is largely used in the printing of linings, either as a white on tinted grounds, or as a solid pigment colour mixed with other pigment colours and fixed with albumen.

(7) Copper Mordants.

The function of copper salts in printing is principally to act as oxidising agents or carriers of oxygen.

Copper Sulphate ($CuSO_4.5H_2O$).—This salt, known as "blue-stone" and "blue vitriol," is manufactured on the large scale by roasting copper pyrites, and afterwards dissolving the residue in hot sulphuric acid. The solution is then filtered from the insoluble matter and treated with scrap iron, which reduces any ferric sulphate, and at the same time precipitates the whole of the copper. The copper is collected, well washed, and re-dissolved in sulphuric acid; then concentrated and purified by repeated recrystallisations, finally coming into the market in the form of beautiful triclinic crystals, containing five molecules of water of crystallisation.

Copper sulphate is used as a constituent of indigo reserve pastes; in Catechu, Logwood, and Sapan wood printing colours; and it enters into the composition of many Aniline blacks, although in those applied by printing it has been replaced by the sulphide and sulphocyanide.

Copper sulphate is the raw material for the preparation of other copper salts.

Copper Sulphide (CuS).—The introduction of copper sulphide as an oxygen carrier in Aniline blacks was due to Charles Lauth in 1864. During the oxidation of Aniline black, either by steaming or ageing in a warm room, the sulphide, in presence of a chlorate, becomes converted into sulphate, and this in turn assists in the oxidation of the aniline. During the printing process the sulphide of copper is inactive, so that the troublesome mishaps attendant on the use of a soluble copper salt are avoided.

As prepared in the works, sulphide of copper is a black paste usually containing 30 per cent. CuS. Either of the following methods of making it may be adopted with equal success:—

I. SULPHIDE OF COPPER.

$$a\begin{cases}1{,}360 \text{ grms. caustic soda } 70^\circ \text{ Tw.}\\ 250 \quad ,, \quad \text{flowers of sulphur.}\end{cases}$$

Dissolve carefully.

$$b\begin{cases}1{,}200 \text{ grms. copper sulphate.}\\ 10{,}000 \quad ,, \quad \text{water.}\end{cases}$$

Mix the two solutions at 170° F., settle, run off the supernatant liquor, and then wash the precipitate three times by decantation. Filter and press the precipitate until it weighs 1500 grms. = 30 per cent. paste. If filtered to 2250 grms. the paste equals 20 per cent. of copper sulphide, a strength at which it is often used on account of its mixing in the printing paste better than the stiffer and drier mass.

II. Copper Sulphide.

$a\begin{cases} \text{1,200 grms. copper sulphate.} \\ \text{10,000 ,, water.} \end{cases}$

$b\begin{cases} \text{1,250 ,, crystallised sodium sulphide.} \\ \text{5,000 ,, water.} \end{cases}$

Mix the two solutions at 170° F., and proceed as in the first recipe.

Copper sulphide is practically used for Aniline blacks only, although it may be sometimes employed in oxidation discharges when other oxygen carriers are not available.

Copper Acetate [$Cu(C_2H_3O_2)_2.H_2O$].—Acetate of copper forms bright green crystals, and can be prepared in solution by the double decomposition of copper sulphate and lead acetate.

$$CuSO_4 + Pb(C_2H_3O_2)_2 = Cu(C_2H_3O_2)_2 + PbSO_4.$$

Copper Acetate 20° Tw.

$a\begin{cases} \text{1000 grms. copper sulphate.} \\ \text{1000 ,, boiling water.} \end{cases}$

$b\begin{cases} \text{1500 ,, lead acetate.} \\ \text{3000 ,, water.} \end{cases}$

Mix *a* and *b*, allow to settle, and set the clear liquor at 20° Tw., or as strong as required.

Acetate of copper is sometimes used as a mordant for Alizarin blue, with which it forms the reddest lake obtainable—a lake of extreme fastness to soap, and very fast to light; as the oxidising agent in Catechu brown, Logwood, and Sapan wood colours, and Aniline black applied by slop padding; and as a constituent of indigo reserve pastes. With the exception of the first application, however, copper nitrate is capable of replacing it with advantage.

Copper Nitrate [$Cu(NO_3)_2.6H_2O$].—Copper nitrate is a powerful oxidising agent. It forms very soluble bluish crystals, and may be prepared in solution by the following recipe:—

Copper Nitrate.

$a\begin{cases} \text{10,000 grms. copper sulphate.} \\ \text{25 litres water.} \end{cases}$

$b\begin{cases} \text{13,200 grms. lead nitrate.} \\ \text{7 litres boiling water.} \end{cases}$

Mix the two solutions hot, allow to settle, and use the clear liquor.

The chief uses of copper nitrate are those given under copper acetate. It is rarely used for Aniline black, which it oxidises too rapidly, and at the same time tenders the cloth.

Copper Sulphocyanide [$Cu_2(CNS)_2$].—Cuprous sulphocyanide was recommended by Higgin in 1868 as a suitable substitute for copper sulphate in Aniline black. It is still used occasionally in England for this purpose, but not so much as formerly, the formulæ for other processes having been perfected to such an extent as to render unnecessary resort to copper salts other than the sulphide. Copper sulphocyanide may be prepared by the double decomposition of copper sulphate and potassium or barium sulphocyanides in presence of a reducing agent like bisulphite of soda. It forms a white insoluble precipitate, generally known as "white paste."

On the whole, the use of copper salts as mordants, in the proper sense of the word, is unimportant. Apart from their application to direct-dyed colours, for the purpose of increasing their fastness to light, and their use for transforming Paranitraniline red into a brown, their value to the calico printer depends

entirely upon their oxidising properties; for although, as already noted, Alizarin blue forms a very permanent lake with copper oxide, this particular shade is not in great demand, and indeed the fact of Alizarin blue forming any such lake is practically unknown.

(8) Lead Mordants.

As mordants proper, lead salts are of no practical value whatever, and are never used as such. Their great importance depends upon their property of forming the brilliant pigments Chrome yellow and Chrome orange, and their usefulness as precipitants in the preparation of other metallic mordants.

Lead Acetate [$Pb(C_2H_3O_2)_2.3H_2O$].—This salt is manufactured by dissolving litharge (PbO) in acetic acid, and is known as "white sugar of lead," or "brown sugar of lead," according to whether pure acid or pyroligneous acid (crude acetic acid) has been used in its preparation.

Basic acetates of lead are obtained by boiling litharge with solutions of the normal salt, and vary in basicity with the quantity of litharge employed. One of the commonest basic acetates of lead is represented by the formula $Pb_2(C_2H_3O_2)_2(OH)_2$. All basic solutions of lead acetate absorb carbonic acid from the air, and become turbid owing to the precipitation of basic lead carbonate.

The basic acetates are for the most part used in the production of plain shades of Chrome yellow on cloth or yarn.

Lead Nitrate [$Pb(NO_3)_2$] is prepared in a similar manner to the acetate, namely, by dissolving litharge in nitric acid. Basic nitrates are prepared by increasing the amount of litharge used, and possess the same properties as the corresponding basic acetates. They give a somewhat redder yellow with bichromate of potash than the latter.

Basic Lead Carbonate.—This constitutes the well-known and largely used pigment white lead. As employed by the calico printer, lead carbonate is prepared by the double decomposition of lead acetate and sodium carbonate.

LEAD CARBONATE.

$\left\{\begin{array}{l}\text{34 kilos. lead acetate.}\\ \text{200 ,, water.}\end{array}\right.$

Precipitate with about—

$\left\{\begin{array}{l}\text{72 kilos. soda-ash.}\\ \text{50 ,, water.}\end{array}\right.$

Settle and wash the precipitate by decantation; then filter it to a 50 per cent. paste.

When required for use the above is simply mixed with starch paste and printed; then developed in bichromate of potash and washed and dried. It is a particularly useful lead colour to use in combination with Aniline black, and gives good yellows in practice.

Lead Sulphate ($PbSO_4$).—This salt is a by-product of many reactions that take place during the making of a large number of mordants by double decomposition. Its only use in calico printing is to act as a mechanical resist to Indigo dye liquors, and for this purpose it is exclusively employed in conjunction with lead nitrate, basic lead acetate, copper salts and china clay.

Plumbite of Soda.—Plumbite of soda is formed when lead hydrate is dissolved in excess of caustic soda. Its chief application is in the discharging of Turkey red by the alkaline process.

In general the lead salts are used as thickened solutions, in which state they

are printed. After passing through a bath of warm sodium sulphate, to prevent them from running, they are treated in a bath of hot bichromate of potash, which not only precipitates the lead as lead chromate (chrome yellow), but at the same time completes the oxidation of any Aniline black, Catechu brown, or Prussian blue that may have been printed along with them. In the latter case, of course, the goods are steamed previous to their treatment in sodium sulphate and bichromate.

In the absence of Prussian blue, the yellow chromate of lead may be transformed into the basic chromate (Lead or Chrome orange) by running the goods through a boiling solution of clear lime water.

The yellowing or tinting of dyed red patterns is usually performed, when Chrome yellow is the colour required, by passing the printed and dyed goods through a solution of basic lead acetate. Then, without drying, they are run through a chamber filled with gaseous ammonia, which precipitates the lead hydrate on the fibre, and afterwards into a bath of bichromate of potash, where the colour is developed. In this way a red pattern on a yellow ground is obtained. Other particulars respecting the *practical* application of lead salts will be furnished in another part of this volume.

(9) Manganese Mordants.

Manganese salts are rarely or never used as true mordants; and although they are capable of forming lakes with mordant colours, they have hitherto not been applied to this purpose in practice. It is worthy of note, however, that the Alizarin blue manganese lake is quite as fast in all respects as the corresponding and largely employed zinc and nickel lakes, and is, moreover, a greener shade than either, so that it might very well form a useful addition to the range of blues obtainable from Alizarin blue.

Manganese Chloride ($MnCl_2.4H_2O$).—This salt is the most generally useful of the manganese compounds. It is obtained as a by-product in the production of chlorine from manganese dioxide and hydrochloric acid, and comes into the market as pink crystals, or as "bronze liquor" marking 71° Tw. The crystals are very hygroscopic, and liquefy if left exposed to the air.

Manganese chloride is used in dyeing and printing for the production of the well-known Manganese brown, bronze, or bistre, as it is variously termed. For this purpose the cloth is padded in a solution of manganese chloride 10°–20° Tw., then passed through a boiling solution of caustic soda free from carbonate, and finally through a weak solution of bleaching powder, which converts the manganous hydrate into manganic oxide (the actual colour). If now the goods are well washed, dried, and treated with aniline salt, a black is obtained. This method at one time formed the basis of several fancy styles in which coloured discharges were produced on a black ground, but is now quite out of date.

Manganese Sulphate ($MnSO_4.H_2O$).—Like the chloride, manganese sulphate is a pink salt. It is also used in the same way for bronzes, and requires no further description.

The acetate, nitrate, and mixtures of these with the sulphate or chloride may be easily prepared by double decomposition with suitable lead salts, but so far these compounds of manganese are of merely scientific interest to the calico printer.

(10) Calcium Salts.

The only calcium salt used as an assistant mordant is the acetate. This is usually prepared in the works by dissolving burnt lime in acetic acid.

Acetate of Lime 23° Tw.

5 kilos. burnt lime (CaO).
25 ,, hot water.

Add gradually to about—

25 kilos. acetic acid 9° Tw.

Add the lime until the mixture is slightly alkaline; allow to settle, and if the filtered liquor is free from iron decant it; if not, add more lime, and settle again, after stirring it up well. When satisfactory, decant the supernatant liquor, wash the precipitate, and add the washings to the strong solution. Then acidify with acetic acid (allow about 2 per cent. excess) and set at 23° Tw.

Other compounds of calcium are chalk, the sulphocyanide, bleaching powder, and the oxalate. Chalk finds its chief employment for neutralising purposes, the sulphocyanide is restricted to the preparation of the corresponding aluminium salt, bleaching powder needs no mention here, and the oxalate is employed solely as an addition to the chromate discharge colours on Indigo.

Oxalate of Lime.—Dissolve 1000 grms. of oxalic acid in water, and neutralise with about 800 grms. of chalk. Wash the precipitate by decantation, and then filter and press it until it weighs 2000 grms. = 50 per cent. $Ca(COO)_2$.

(11) Oil Mordants.

The value of fatty matters in dyeing has been recognised from time immemorial. The particular fatty substance used by the ancient Hindoos in their process of Madder red dyeing was derived from milk. They steeped the cotton cloth in milk and then spread it out in the sun to dry, repeating the operations until it was sufficiently impregnated with fat to fix the required amount of alumina in the fibre when steeped in a solution of alum or some preparation of alum. At the present time an analogous treatment is observed in many styles, and in the modern process of Turkey-red dyeing, the impregnating of cloth with a fatty matter is no less essential or characteristic a feature than in the old Hindoo process. The fatty matters used to-day are vegetable oils, modified in such a way as to render them soluble in water, but their function is the same as that of milk; and although a good deal of profound research work has been carried out with the object of elucidating their exact rôle, the chemical changes that they undergo during the various processes of steaming, mordanting, and dyeing are still subject to contention, and their nature is as yet more or less a matter of opinion.

Whatever the nature of these chemical changes may be, it is beyond all dispute that they enable the oil to attract the mordant and fix it upon the fibre; so that, practically, the fatty matter acts as a fixing agent, and, like other fixing agents, it forms a component part of the ultimate colour lake produced upon the cloth. Further than that, certain oils play the part of true mordants towards basic colouring matters; and if the resulting lakes are not very fast, they are at least a combination of fatty acid with colour bases, and are fixed upon the fibre in a similar way to all other colour lakes. Sometimes, as in the last instance, the oil, or at least the fatty acid, acts the part of mordant, the metallic salt with which it is combined simply acting as a fixing agent; at other times the reverse is the case, the metallic base playing the rôle of mordant, and the fatty acid that of fixing agent. In Turkey red the fatty matter forms an insoluble compound with the alumina of the mordant, and this insoluble body further forms a coloured lake with Alizarin. If the fatty acid

is absent, the full brilliancy of the red cannot be obtained by any means; and if the alumina is absent, no red at all is obtained. From this it is evident that the presence of both elements is essential; and such being the case, it is only reasonable to infer that oil and alumina in combination constitute a *compound* mordant, and that the oil is just as important as the alumina, although the latter is the real base of the colour lake. Cloth mordanted for Turkey red can also be dyed in basic colours, the oil then acting as mordant, so that with mordant colours (Alizarin and others of phenolic type) the metallic base of the fatty compound is the mordant, and with basic colours (Methylene blue, Magenta, etc.) the fatty element is the mordant.

For these reasons oil preparations have been called oil mordants; and as their importance as such is universally recognised, it only remains to consider their preparation and application in practice.

The chemistry of the subject is too complex to treat adequately in a brief notice like the present, and therefore the following remarks will be confined to the practical aspect of oil mordants. Further particulars respecting the theory of the subject are easily obtainable from the many works dealing specially with the question of the chemical technology of oils, fats, and soaps; and to such works as these the reader is referred for concise chemical data.

Castor Oil.—The basis of most oil mordants used at the present time is castor oil, the essential constituent of which is the glycerin compound of ricinoleïc acid, the composition of which is represented by the formula $C_3H_5(O.C_{18}H_{33}O_2)_3$. When boiled with caustic soda or sodium carbonate the oil is decomposed, with the formation of the sodium salt of the ricinoleïc acid and the liberation of glycerin.

$$3NaOH + C_3H_5(O.C_{18}H_{33}O_2)_3 = 3NaO.C_{18}H_{33}O_2 + C_3H_5(OH)_3.$$

Ricinoleate of soda is the well-known castor-oil soap or soluble oil, and is used as such for the preparing of cloth for the steam style of printing. More frequently, however, an ammonio-soda-soap is employed for this purpose, as the ammonia volatilises on drying the padded cloth, leaving free fatty acid on the fibre. On treating castor-oil soap with mineral acids the ricinoleïc acid is set free, and can then be combined with ammonia and soda in any required proportions; or ammonia and soda soaps can be made separately and mixed as desired.

In practice the following method of preparing ricinoleïc acid has been in use for many years:—

RICINOLEÏC ACID.

40 kilos. castor oil.
28 ,, caustic soda 70° Tw.
80 ,, water.

Boil together (adding water to replace that evaporated) until a few drops of the soap give a perfectly clear solution with cold water; then neutralise with about

15 kilos. sulphuric acid 168° Tw.
100 ,, water

and boil again until the floating mass of fatty acid becomes quite thick. Now allow the solution to stand some time, then draw off the watery portion, and wash the fatty acid two or three times with hot water. Finally, draw off all the water and collect the fatty acid.

From the above ricinoleïc acid a prepare for steam Alizarin reds and pinks is made as follows:—

Oil Prepare for Reds and Pinks.

500 grms. ricinoleïc acid.
200 ,, titrated ammonia.
200 ,, ,, sodium carbonate solution.
100 ,, water.

1000 grms.

This equals 50 per cent. fatty acid.

For reds and pinks printed together the cloth is passed, before printing, through the above solution reduced to 5 per cent.; for pinks alone, $2\frac{1}{2}$ per cent. fatty acid is sufficient.

Titrated Soda and Ammonia (for above).

For the soda take 133 grms. soda-ash per litre.
For the ammonia take 689 grms. ammonia 6 per cent. per litre.

20 c.c. of either solution ought to neutralise 43·4 c.c. $\frac{N}{1}H_2SO_4$.

A slight excess of ammonia is not injurious, but it is unnecessary in any oil prepare.

Although the ricinoleates are of great practical utility, they are not considered to give results equal to those obtained by the use of the *sulphoricinoleates*, and, in consequence, the latter are by far the most commonly employed both for printing and dyeing.

On the large scale the preparation of sulphoricinoleïc acid is carried out in double-cased lead-lined pans, fitted with lead agitators and draw-off taps. A constant stream of cold water circulates between the casings, and serves to keep the temperature of the contents below 30° C., above which a quite different reaction is apt to take place, to the utter destruction of the oil mordant as such. Castor oil is placed in the pan, and concentrated sulphuric acid is allowed to trickle into it slowly through a glass tube. The mixture is stirred the whole time, and when all the acid has been added it is allowed to stand overnight—or longer in winter—to complete the reaction. The product is then well washed with brine, and either neutralised in the pan or drawn off for treatment elsewhere.

In practice, the following proportions have given good results; but the quantity of sulphuric acid is subject to modification according to the time of year at which the oleine is made. In winter and cold weather it is frequently necessary to use as much as 40 to 50 per cent. of sulphuric acid calculated on the weight of oil.

Sulphoricinoleïc Acid.

To 40 kilos. castor oil, add slowly at not above 30°–35° C.
10 ,, sulphuric acid 168° Tw.

Allow to stand 12–24 hours and then wash by decantation with—

$\left\{\begin{array}{l}\text{120 kilos. water at 35° C.}\\ \text{12 ,, common salt or Glauber salt.}\end{array}\right.$

Run the wash-water from under the fatty acid and repeat the washing twice, with the same proportions of salt and water. Finally allow all the fatty acid to rise to the surface and then skim it off or run off the water beneath it. Yield = 53 kilos.

Sulphoricinoleate of Soda—Oleine, etc.

250 grms. of the above acid.
500 ,, water.

Add about—

150 grms. caustic soda 15° Tw. until the solution is just slightly alkaline, then add water to make up to 1000 grms.

———

1000 grms.

This equals 25 per cent. fatty acid.

The above may be used for Turkey-red dyeing and for various other purposes including the preparation of compound tin mordants, which are employed extensively in chintz printing and other steam styles. The ammonia salt may be made in a similar way.

Sulphoricinoleate of Ammonia, 25 per cent.

250 grms. sulphoricinoleïc acid.
500 ,, water.
110 ,, ammonia (6 per cent. NH_3).
140 ,, water.

———

1000 grms.

In addition to the simple alkaline salts of the above fatty acids it is in many instances advantageous to make use of their stannous and stannic compounds, especially where particularly bright colours are desired. The tin sulphoricinoleates are soluble in ammonia and can therefore be applied to the cloth without difficulty. As a rule they form about 2 per cent. of the total fatty bodies present in a prepare, but they may be increased if occasion demands, although if too great a quantity be used the white ground of the printed cloth is apt to become yellow.

Stannous Sulphoricinoleate.

50 kilos. sulphoricinoleate of soda, 25 per cent.

Heat to 40° C. and add slowly, stirring all the time—

3·2 kilos. stannous chloride.
20 ,, cold water.

A slight excess of stannous chloride is advantageous. Filter off to 17·8 kilos. = 35·6 kilos. of paste from 100 kilos. oleine.

The ammonio-stannous salt is made by adding the above to ammonia oleine, and the stannic compound by precipitating the fatty acid from sulphoricinoleate of soda with oxymuriate of tin.

Ammonio-stannous Sulphoricinoleate.

250 grms. sulphoricinoleïc acid.
250 ,, stannous sulphoricinoleate.
300 ,, cold water.

Add about—

120 ,, ammonia 6 per cent. and make up with water to

———

1000 grms.

Stannic Sulphoricinoleate.

1000 grms. sulphoricinoleate of soda 25 per cent.

Add gradually, stirring all the time—

90 grms. oxymuriate of tin.

Wait a little after each addition, and guard against an excess of tin at any one time, otherwise the product separates out badly.

1000 grms. of the soda oleine 25 per cent. = 375·5 of the tin salt.

In using these tin compounds for preparing calico for the steam style they are mixed with the ordinary oleines in the first instance, and then reduced with water to the proper strength, a sufficiency of ammonia being added to dissolve the tin compound, or Tin Oil. Thus for steam work containing heavy Alizarin reds the following mixture is used for preparing the cloth :—

5 per cent. TIN OIL PREPARE.
20 kilos. of Tin Oil, 25 per cent.
Reduce with water and ammonia to make
100 kilos.

This mixture contains 5 per cent. fatty acids.

TIN OIL, 25 per cent. (for above).

980	grms.	sulphoricinoleate of soda, 25 per cent.
20	,,	stannous sulphoricinoleate.
1000		

Sulphoricinoleate of soda may be replaced by the corresponding ammonia salt, either wholly or in part, and castor-oil soda soap (ricinoleate of soda) may also be employed with satisfactory results.

One of the most important stages in the dyeing of Alizarin reds is the oiling and steaming of the goods after dyeing. The object of this is to brighten the red, and it may be attained by using any of the ordinary oleines or soluble oils, especially if they contain a little oxalic acid. A much better result, however, is obtained by using one or other of the following oil prepares.

BRIGHTENING OIL FOR MADDER REDS I.

200	grms.	sulphoricinoleate of soda 25 per cent.
15	,,	ammonio-stannous sulphoricinoleate.
125	,,	oxalate of ammonia 3° Tw.
660	,,	water.
1000	grms.	= 5 per cent. fatty acids.

BRIGHTENING OIL FOR MADDER REDS II.

200	grms.	sulphoricinoleate of soda 25 per cent.
3	,,	oxalic acid.
$2\frac{1}{2}$	,,	stannous chloride.
600	,,	water and enough ammonia and water to dissolve the precipitate and make up to—
1000	grms.	= 5 per cent. fatty acids.

The dyed cloth is padded in either of the foregoing solutions, then dried, steamed for an hour at 15 lbs. per sq. in. pressure, and then washed and soaped. The oil enters into combination with the colour lake, which ultimately consists of Alizarin, alumina, tin, and fatty matter.

The presence of oily or fatty compounds on the fibre intensifies the depth and increases the brilliancy of the majority of colouring matters used in calico printing, and for this reason almost all goods are now prepared in oleine before printing, the chief exceptions being those upon which patterns are printed in alumina and iron mordants. These goods have to be dyed after printing, and if the cloth contained any fatty matter this would attract dyestuff to the white parts of the cloth and thus stain them, possibly beyond remedy. Hence the oil is applied after dyeing as described above.

Olive Oil was at one time used exclusively for the preparation of oleines, soluble oils, etc., and is still largely employed for dyeing the best Turkey reds. Its price prevents its general application now that castor oil has been found equally suitable for most classes of work. Many experiments, on an industrial scale, have been made, with the hope of substituting a cheaper oil for olive oil in Turkey red works, but so far but little success has attended these efforts. Castor oil and cotton-seed oil both yield bright, even brilliant, reds, but they do not possess the extraordinary fastness to light, soap, and acid that is associated with the old-fashioned Turkey red on an olive oil prepared foundation, neither are they so rich and full in appearance. For high-class Turkey red, therefore, olive oil is still the fatty matter *par excellence* to use.

In the old processes of Turkey-red dyeing the cloth was repeatedly treated in an emulsion made from olive oil and a weak solution of soda or sheep-dung. After each padding it was hung in a hot stove or chamber to dry and age. During the successive paddings and ageings the oil became transformed into a substance capable of combining with alumina mordants, and the oleate of alumina (?) thus formed was in turn capable of combining with Madder or Alizarin to form Turkey red. What the nature of the chemical changes undergone by the oil in ageing really is cannot be affirmed with certainty, but it is probably transformed into oxyoleïc acid by the combined action of heat and air. That some process of oxidation takes place is generally admitted, and this fact has led to many attempts at hastening the process. Beyond noting that various oxidising agents were added to the oil itself, and that the oil was oxidised before use by treatment with chlorine, etc., it is unnecessary to go into these old methods, since they are now rarely, or never, employed. Steiner impregnated the cloth in hot, pure olive oil, then dried it at 70° C., and afterwards treated it in weak solutions of soda, stoving after each treatment for two hours at 75° C.; in this way he shortened the process, but even this short process has had to give way before the oleine process, which, when properly worked, yields reds equal to any hitherto produced.

The manufacture of oil mordants of all descriptions from olive oil is identical with that of similar mordants from castor oil; in fact, the only difference between the two series of compounds is that due to the slightly different composition of olive oil.

Olive oil consists essentially of the glycerin compound of oleic acid, which contains three atoms less of oxygen than the corresponding glycerin compound of castor oil. In addition, olive oil contains *tripalmitin*, and it is not unlikely that this may account for the superiority of olive oil over castor oil for Turkey-red work, or at least influence the result in some way, for it is not uncommon for complex bodies to produce the fastest colour lakes.

When shaken up with dilute solutions of alkali, olive oil is not saponified, but forms the emulsion already mentioned, in which it exists in an extremely fine state of division. The quality of oil best adapted for this purpose is that obtained at the second extraction of oil from the fruit; the product obtained at the first extraction by pressing the ripe fruit in the cold is known as "virgin" or "cold drawn" oil, and is the purest and most highly esteemed quality for food and burning. The oil obtained at the second extraction, by the aid of heat and great pressure, and after the husks and crushed fruit have been steeped in boiling water and piled in heaps until a kind of fermentation has occurred, gradually becomes rancid (*rancid Gallipoli*, Fr. *huile tournante*), owing to the liberation of the free fatty acids, and is the quality most suitable for Turkey-red dyeing. The presence of free stearic, oleïc, and palmitic acids, together with a certain amount of nitrogenous organic matter, promotes

the rapid formation of a more or less permanent emulsion, and is found by experience to ensure the fastest and brightest reds.

An emulsion that is in general use for Turkey-red dyeing by the old process is the following:—

OLIVE OIL EMULSION 6 per cent.

$$\begin{cases} 60 \text{ kilos. common olive oil.} \\ 39 \quad ,, \quad \text{soda crystals } (Na_2CO_3.10H_2O). \\ 100 \quad ,, \quad \text{water.} \end{cases}$$

Mix well until thoroughly emulsified, and then add sufficient water at 50° C. to make up the whole to 1000 kilogrammes. If the emulsion tends to separate, add more sodium carbonate, or about 10 kilos. of cow-dung, until it remains permanent some twelve to sixteen hours. The emulsion can be strengthened or diluted according to circumstances.

Boiled with caustic alkalies or alkaline carbonates, olive oil is saponified in the same way as castor oil, but the soap is not used as a mordant, although it possesses a very similar composition. It consists essentially of sodium or potassium oleate, and its close resemblance to castor-oil soap is evident on comparing their respective formulæ,—

$C_{18}H_{33}O.ONa$.	$C_{18}H_{33}O_2.ONa$.
Olive-oil soap.	Castor-oil soap.

Olive-oil soda soap, known better as Marseilles Soap, is largely used for the after-soaping of Turkey-red dyed goods, and, where not too expensive, for ordinary printed goods of all descriptions. Its advantages are, that it is a dependable article, regular in composition, and neutral.

By acting on olive oil with strong sulphuric acid in the cold, analogous compounds to those prepared from castor oil under the same conditions are obtained. These bodies combined and neutralised with soda or ammonia constitute the olive oil oleines, sulphated, soluble, and Alizarin oils of commerce. As previously noted, they are suitable for all purposes to which such compounds are applied, but their cost limits their use to Turkey-red dyeing; and although they are occasionally used for preparing steam work, they offer no advantages in this direction over corresponding castor oil preparations.

The manufacture of olive oil oleins is identical with that already described for the manufacture of the castor oil compounds, and the various tin oleates can be similarly produced.

The practical application of olive oil will be dealt with in connection with the dyeing of Turkey red.

Most of the oxidised oils, to which a slight allusion has already been made, are of little practical interest, and if used at all, are used to a very limited extent. One compound, which may perhaps be classed amongst them, is, however, largely employed by the calico printer in the production of steam Alizarin reds. It is generally known as "chlor oil," and consists of a mixture of olive oil with bleaching powder solution.

CHLOR OIL.

100 kilos. of olive oil.
100 litres of bleaching powder solution 7·2° Tw. (= 25 grms. active chlorine per litre).

Stir well together until the emulsion is homogeneous.

In place of olive oil, the cheaper cotton-seed and rape-seed oils may be used with advantage; in fact, these two oils are perhaps as often employed as olive oil at the present time.

Oleines prepared from cotton-seed and rape-seed oils possess different properties from those made from olive and castor oils. They do not dissolve in water, but only form a sort of emulsion; neither do they lend themselves to the production of the best qualities of Turkey red. At the same time they are used for this purpose, a cotton-seed oil prepare, containing a little cow-dung and an excess of sodium carbonate, being frequently employed in the same way almost as ordinary olive oil emulsions, except that the goods are steamed instead of being stoved. This prepare may be made up as follows:—

6 per cent. COTTON-SEED OIL PREPARE (for Turkey red).

To $\begin{cases} \text{60 kilos. cotton-seed oil add gradually—} \\ \text{10 ,, sulphuric acid 168° Tw.} \end{cases}$

Allow to act (in the cold) 12–24 hours; then neutralise with caustic soda and add—

$\begin{cases} \text{12 kilos. soda-ash.} \\ \text{10 ,, cow-dung.} \\ \text{500 ,, water.} \end{cases}$

Stir well to emulsify properly, and, finally, add sufficient water to bring the whole up to 1000 kilogrammes.

Goods prepared in this solution are steamed after drying, allowed to lie in pile a day or two, and then lightly washed through dilute sodium carbonate ($1\frac{1}{2}$° Tw.) and water, after which they are mordanted and dyed as usual.

The red produced in this way is very bright, but it does not resist the action of mineral acids so well as that resulting from the use of olive oil, neither does it possess the same fullness of shade nor fastness to energetic soaping.

The chief use of cotton-seed oil is for soap-making, and for adding to boiled starch thickenings for the purpose of softening them. Most of the cheap colour oils consist of either cotton-seed or rape-seed oil, both of which are suitable substitutes for olive oil in boiled thickening pastes.

Other Oil Preparations.—Various modifications of oleïc, ricinoleïc, and sulphoricinoleïc acids have been suggested as additions to steam Alizarin reds and pinks for the purpose of eliminating the preliminary preparation of the cloth with oleine or soluble oil. Of these modifications perhaps the best are LIZAROL D, SPENCOL, RED OIL, and other products of similar constitution. They consist essentially of the compounds resulting from the condensation of formaldehyde with ricinoleïc and other fatty acids. Being insoluble in water, they have no action in the cold on the metallic mordants and colouring matters with which they are associated in printing colours; but, under the influence of steam, they dissociate and gradually combine, on the fibre, with both mordant and colouring matter, to form very fast lakes.

For small sprig patterns, shirtings, and the like, in which the greater part of the cloth is left unprinted, and in multicolour patterns containing very little red and pink, the use of oil mordants of the Lizarol type effects considerable saving in cost of production.

On the other hand, large masses of colour containing such oil mordants are exceedingly apt to " mark off " (or be transferred to the unprinted portions of the cloth) during the soaping operations after steaming, and at all times they are liable to scum in printing. For anything but lightly engraved patterns, therefore, it is preferable to prepare the cloth before printing.

(12) Tannic Acid.

The use of tannic acid (the astringent principle of myrobalans, sumach, valonia, gall nuts, divi-divi, etc.) as a mordant depends upon its property of

forming insoluble coloured precipitates with the colourless or leuco bases of basic aniline dyestuffs. During this reaction the mineral or organic acids combined with the colour base in the dyestuff are liberated, and if not neutralised in some way, they tend to redissolve the coloured precipitate or lake. Even an excess of tannic acid forms soluble compounds with basic dyestuffs; hence, in order to obtain insoluble compounds, it is essential to neutralise all free acid whatsoever. This may be done by adding sodium carbonate to the mixed solutions, or to one of them, before the precipitation is effected, but in practice it is found better, in every way, to precipitate the tannic acid on the cloth as an insoluble metallic tannate, the metallic base of which combines, more or less, with the liberated acids. These insoluble tannates possess quite as great an affinity for the leuco bases of colouring matters as does the free tannic acid, and the compounds they form possess the additional valuable quality of being much faster to soaping than the simple compounds of tannic acid and colour base.

As is well known, tannic acid produces insoluble salts with aluminium, iron, tin, chromium, and other metallic salts; and consequently cloth mordanted with any of these tannates can be dyed in either basic colours or in mordant colours, like Alizarin, Logwood, etc. This dual character of tannic acid as fixing agent and mordant is of the utmost value, and is taken advantage of in many styles of work. Tannate of iron is a blackish precipitate, which is sometimes made to serve as a grey self colour, and thus tannic acid may, in a sense, be considered as a colouring matter in addition to its other uses. In this capacity, however, it is rarely employed (except in the manufacture of inks), its chief use being to tone or darken other colouring matters that are dyed upon it, and are fixed upon the fibre as tannic acid or iron lakes, according to the class of colouring matter employed.

The cotton fibre possesses the property of abstracting tannic acid from its solutions; and so great is its power in this respect that it will retain the whole of the tannic acid it has absorbed from a 5 per cent. solution when it is afterwards steeped in weaker solutions. As a matter of fact, J. Koechlin has ascertained that it will even absorb additional tannic acid from a 2 per cent. solution, and will only begin to part with it in a solution reduced to ·02 per cent. of tannic acid.

Although the steeping method of mordanting is used for dyeing yarn and calico, the most expeditious method of applying tannic acid to the fibre of woven cotton fabrics is by padding in a mangle, as practised by the calico printer to the exclusion of all other methods. Padding entails the use of very much stronger solutions than steeping, but at the same time a correspondingly small volume of liquor can be used, so that while the process is accelerated, no extra expense for material is incurred. After padding, the cloth is immediately dried over copper cylinders or in hot air, and can then be passed into the fixing bath without any risk of the tannic acid dissolving off and forming a useless precipitate in the bath.

The usual fixing agent for tannic acid is tartar emetic (or other salts of antimony), though, as noted above, other metallic salts are capable of forming insoluble tannates, and are utilised for the purpose in special cases. The tannate of antimony is white, and quite insoluble in water, qualities which render it peculiarly adapted to the production of bright shades; it is precipitated easily in the cold, especially in the presence of common salt; and it dissolves in concentrated caustic soda,—a property which allows of white designs being produced on a dyed basic colour ground.

In mordanting cloth for printing and dyeing, the following method may be employed with good results:—

(1) Pad the cloth through a 5 per cent. tannin solution.

5 per cent. TANNIN MORDANT.

50	grms.	tannic acid.
50	,,	common salt.
900	,,	water.

(2) Dry the goods and fix the mordant by running through a 2 per cent. solution of tartar emetic and chalk at 40° C.

2 per cent. FIXING LIQUOR.

20	grms.	tartar emetic.
20	,,	chalk.
960	,,	water.

The chalk is added to neutralise the acidity of the acid potassium tartrate [$C_4H_4O_4(OH)(OK)$] which gradually accumulates as the antimony is taken up by the tannic acid.

(3) Well wash the cloth and then dry it. It may then be dyed at once or printed in caustic soda, steamed, washed, and dyed in basic colours.

Another method of fixing tannic acid on the fibre is first to print an iron or aluminium mordant, age and dung it as usual, and then dye it up in tannic acid or any of the vegetable tannin matters—say sumach, for instance. The tannin is fixed on the printed parts of the cloth as an insoluble tannate of iron or alumina, and after soaping, to clear the unprinted portions, it can be dyed up in any required basic colour, thus giving a coloured pattern on a white ground. The same effect can be produced by printing a thickened solution of tannic acid, fixing it in tartar emetic, and dyeing afterwards; also by printing a mixture of aluminium sulphate or alum, acetic acid, tannic acid, and ammonium chloride. The latter is not essential, but aids the fixation. Print, steam, and dye.

5 per cent. TANNIN MORDANT.

50	grms.	tannic acid.
10	,,	ammonium chloride.
100	,,	water.

Dissolve and add—

10	grms.	aluminium sulphate.
75	,,	acetic acid 9° Tw.
50	,,	water.
705	,,	gum-tragacanth thickening.

Before steaming, the tannic acid does not unite with alumina in the presence of the acetic acid, but when the latter is volatilised the precipitation takes place in the fibre, and it suffices simply to wash the goods before dyeing. A better result is obtained by a supplementary fixation in a dilute solution of tartar emetic; in which case the alumina exerts a beneficial influence on the brightness of the ultimate colour, which is also faster than if no alumina were present. By replacing the gum tragacanth with water the solution may be used for ordinary mordanting for printing in caustic soda, as above. The ammonium chloride [1] then prevents the caustic soda scum on the printing roller from injuring the parts of the cloth which are intended to retain the mordant and form the coloured ground when dyed. After printing, the goods are passed through the rapid ager, fixed in tartar emetic (if desired), washed and dyed.

The fact that tannates of basic colours are soluble in excess of acid is taken advantage of in the printing of steam colours. A thickened paste containing acetic acid, a little tartaric acid, tannic acid, and basic colouring matter is printed on white cloth. The cloth is then dried and steamed, when the acetic

[1] If the mordanted goods are dried over copper cylinders it is better to use ammonium sulphate as an anti-scumming agent. Ammonium chloride dissociates on the cylinders, dissolves copper, and gives rise to brown stains of copper tannate.

acid is driven off and the tannic acid combines with the colouring matter to form an insoluble lake, which is rendered still more insoluble by a passage through tartar emetic and chalk, whereby the still remaining tartaric acid is neutralised and an insoluble double tannate of antimony and colour base is produced.

For dark shades of blue, green, brown, etc., any of the vegetable tannin matters can be used in all cases where their colour does not detract from that required ; but for light shades, tannic acid itself is always preferable, since, in the qualities specially prepared for this class of work, it possesses very little colour—at most only a pale yellow tint.

(13) Katanols.

Three new mordants for basic dyestuffs under the name of Katanol have been introduced successively during the past twelve years. In many respects they may be regarded as Sulphur dyestuffs, being prepared by a process similar to that employed in the manufacture of those colouring matters and possessing many of their properties. In all probability the fact that many Sulphur colours act as mordants for basic colours suggested the idea of preparing analogous products with the same mordanting property but free from the drawback of dyeing the fibre. The Katanols fulfil these conditions in a satisfactory manner for many purposes, but they are none of them quite free as yet from the defect of staining the fibre.

Katanol O., the first of the group, was introduced by the Farbenfabriken vorm. F. Bayer & Co., in 1922. It is prepared by fusing sulphur with *o*-chlorophenol and comes into the market as a pale yellow powder, insoluble in water and acids but soluble in a dilute solution of soda-ash. All acids precipitate it from its alkaline solution.

Katanol W. is a soluble derivative of Katanol O., which it resembles closely in general properties. It is readily soluble in water, from which it is precipitated *only* by mineral acids or strong organic acids ; weak organic acids, such as acetic and formic acids, do not precipitate it unless in excess.

Katanol O.N. represents an improved quality of Katanol O., over which it possesses the advantages of requiring less soda-ash for its solution and of leaving the fabric practically unstained. It is the latest of the series and has virtually replaced the two earlier members.

The chief points advanced in favour of employing Katanols in place of tannic acid as mordants for basic colours on cotton are (1) that they are applied by a single simple process of dyeing or padding and, unlike tannic acid, require no further treatment for their fixation on the fibre, (2) that they are unaffected by iron salts or rust, which blacken tannic acid, and (3) that they yield brighter shades, which are faster to washing.

On the other hand, the Katanols cannot be used in the direct printing of basic colours because, under any practical conditions, they combine with the colouring matter too rapidly, precipitating almost at once, an insoluble lake which cannot be satisfactorily printed and fixed on the cloth. Consequently, so far as printing styles are concerned, their employment is limited to the production of basic colour resists under Aniline black and of basic colour discharge effects on dyed grounds of substantive and Azoic colours. Moreover, all Katanols impart a perceptible yellow tinge to the cloth, which impairs the purity of the whites in discharge and resist work, unless it be neutralised or masked by the application of a white plastic substance in printing. The Katanol lakes of basic colours, too, are not so fast to light as those obtained with tannate of antimony, and although they are said to be faster to washing, this particular feature has not been so generally appreciated as to prejudice the consumption of tannic acid by printers.

Application.—In the production of Aniline black resist styles the goods are padded with a 1–1¼ per cent. solution of Katanol O.N. and, after drying, are re-padded with the Aniline black liquor in the usual way. The first padding solution may be made up as follows:—

12	grms.	Katanol O.N.
1·2	,,	soda-ash.
10	c.c.	oleine 40 per cent.
990	,,	water (boiling).
1000	c.c.	

Mix the Katanol with the soda-ash, add the oleine, and finally pour the boiling water over the whole, and stir till dissolved.

When mordanting cotton piece goods for producing basic colour discharge effects on substantive or azoic colour-dyed grounds, the already dyed pieces may be padded in a 2 per cent. solution of Katanol made up on the lines indicated above. In the case of substantive or direct colour grounds, however, it is preferable to add the Katanol directly to the dyebath (about 2 per cent. on the weight of the goods if dyed on a jigger), thus saving a process by dyeing and mordanting simultaneously. With Azoic colour grounds, or those produced with developed direct colours, this latter method is not suitable and the former must be adopted.

(14) Various Assistants and Preparations.

It is impossible to give even the briefest description of every substance used in calico printing, and, therefore, only the most important have, so far, been dealt with; but there exist many others that will be mentioned in the following pages. Of these some are too well known to require any detailed description, and others are only used occasionally or for special processes. Amongst the former may be classed the various salts of soda and potash, chalk, lime, the various acids, bleaching powder, alcohol, ether, glycerin, glucose, malt, turpentine, benzene, carbolic acid, borax, ammonia, wax, etc., all of which are common articles of commerce. While not entering into any discussion of their general properties or modes of manufacture, their special functions will be pointed out in all cases where they play an essential part in any process given in the following pages, and not already explained. This will prevent needless repetition, and will allow of each style of printing being treated as a whole, without the necessity of referring to all parts of the volume at every turn.

The most important preparations that have not been given include vanadium chloride, magnesium acetate, the citrates of soda and ammonia, Chrome yellow and orange, Prussian blue, soda chemick, nitrate of ammonia, and ammonium oxalate.

(1) **Vanadium Chloride** (VCl_2) is a blue solution used as an oxygen carrier in Aniline black printing and dyeing. It may be made according to the following recipe:—

VANADIUM CHLORIDE SOLUTION, 1 per cent.

10	grms.	vanadate of ammonia (NH_4VO_3).
70	,,	hydrochloric acid 30 per cent.
40	,,	water.
7	,,	glycerin.

Heat until a pure blue is obtained; then make up with water to 1000 grammes. A solution one-tenth of this strength (1 : 1000) is usually employed in practice, and can be reduced from stock as required.

(2) **Magnesium Acetate** [$Mg(C_2H_3O_2)_2$] finds its chief use as a resist for

Aniline black. It yields brighter colours than sodium acetate, by reason of the fact that magnesium oxide does not injure the colours to the same extent as sodium hydrate during the reaction brought about in steaming.

MAGNESIUM ACETATE 32° Tw.

1000 grms. magnesium carbonate.
4000 ,, acetic acid 9° Tw.

Add the magnesium salt to the acid gradually and until it is slightly in excess, then heat gently until the filtered liquor contains no trace of iron; decant, filter, and saturate with acetic acid.

Of other magnesium compounds that are used occasionally in printing and its allied textile industries, the following are the most important:—

Magnesium Oxide, *Calcined Magnesia* (MgO). This is a white, amorphous powder, insoluble in water but readily soluble in acids. It may be employed like zinc oxide as a resist under Aniline black, and also as the basis for the preparation of various magnesium salts. Its chief use, however, is as a neutralising agent for acids in cases where an excess of a stronger and soluble alkali would be injurious.

Magnesium Carbonate, *Magnesia Alba* ($MgCO_3$). This comes into the market as a light, white powder, or in the form of extremely light friable bricks (or lumps), either of which forms may contain magnesium hydrate, according to the method of manufacture. A good quality must be pure white and free from iron. Magnesium carbonate is practically insoluble in water to which it, nevertheless, imparts a slightly alkaline reaction. Like the oxide, magnesium carbonate may be used as a resist under Aniline black, and also to neutralise acids, but it serves mainly in printing as the raw material for the manufacture of magnesium acetate.

Magnesium Sulphate ($MgSO_4.7H_2O$), better known as *Epsom Salts*, is obtained largely as a by-product of the potash industry and from *kieserite*, a native magnesium sulphate ($MgSO_4.H_2O$). Commercial magnesium sulphate occurs as very small colourless crystals which in bulk have somewhat the appearance and feel of finely ground meal. These crystals are extremely soluble, 1 part of $MgSO_4.7H_2O$ dissolving in 3 parts of cold water, and in $1\frac{1}{2}$ parts of boiling water. Magnesium sulphate is employed extensively in the cheaper kinds of cotton finishing, but, as it attracts moisture from the air, its use in this way, for weighting purposes, is a fruitful cause of complaint.

In bleaching silk with sodium peroxide an addition of magnesium sulphate is often made to the strongly alkaline solution of peroxide in order to replace its injurious causticity by the harmless alkalinity of sparingly soluble magnesium hydrate. For the same reason, magnesium sulphate is used as a corrective in alkaline finishing pastes. It also finds some application, along with borax and other salts, in the production of uninflammable finishes.

Magnesium Chloride ($MgCl_2.6H_2O$). This is obtained on the large scale as a waste product in the production of potassium chloride from the mineral *carnallite*. It is deliquescent and very soluble in water. On being heated, the damp salt is converted into magnesium oxychloride and free hydrochloric acid. This property renders magnesium chloride valuable as a carbonising agent in the shoddy trade for the removal of cotton from wool-cotton union goods, but condemns its use by spinners as a hygroscopic ingredient in sizes applied to cotton warps that are intended to be woven into printing cloths. It is, however, still too often so used by spinners who are ignorant of (or ignore) its disastrous effects. All printing cloths are singed before bleaching, and if by chance a cloth contains magnesium chloride the fibre is tendered to the point of destruction by the hydrochloric acid liberated during the passage of the goods over the red-hot plates or the gas flames of the singeing machine.

(3) **Citrates of Soda.**—These salts, in varying degrees of acidity, are largely used as resists under iron and aluminium mordants, and under steam Alizarin pinks. They act by preventing the precipitation of the insoluble basic salts and oxides during the ageing and steaming processes; and are prepared by dissolving citric acid in caustic soda.

	I.	II.	III.	IV.
Citric acid	120	120	120	120 grms.
Caustic soda 71° Tw. . .	70	140	210	245 ,,

I.	$C_3H_4(OH)(CO_2H)_2(CO_2Na)$	very acid salt.
II.	$C_3H_4(OH)(CO_2H)(CO_2Na)_2$	acid ,,
III.	$C_3H_4(OH)(CO_2Na)_3$	neutral ,,
IV.	(,, ,,) + ½ molecule NaOH	alkaline ,,

Mixed with China clay, sodium chlorate, and yellow prussiate of potash, these citrates are employed in oxidation discharges on a great variety of dyed grounds.

(4) **Citrate of Ammonia** [$C_3H_4(OH)(COONH_4)_3$] is prepared by dissolving finely ground citric acid in cold ammonia in a covered cask.

Citrate of Ammonia 20° Tw.

200 grms. finely ground citric acid.
500 ,, ammonia 20 per cent. NH_3.
300 ,, water.

Dissolve, and add a little water to bring the solution down to 20° Tw.

Citrate of ammonia is used like the citrates of soda for all kinds of resists and discharges. On steaming it dissociates, leaving the free acid on the fibre —an essential in some classes of work.

The *tartrate* is made in the same way and is used for the same purposes.

The *oxalate* is a somewhat insoluble salt, made by mixing solutions of oxalic acid and ammonia in proper proportions. It crystallises out at a strength above 3° Tw., and is mainly used as an addition to brightening oils for Alizarin-dyed reds.

(5) **Nitrate of Ammonia** (NH_4NO_3) is a well-known salt. In practice it is prepared by neutralising ammonia with nitric acid.

Nitrate of Ammonia 32° Tw.

8,500 grms. ammonia 20 per cent.
Add gradually—
12,000 ,, nitric acid 66° Tw.
Neutralise, and set at 32° Tw.

A thickened solution of the above when printed on tannin-mordanted cloth resists the action of an over-print of caustic soda, and preserves the tannin under it from being discharged by the caustic soda cover. The same paste printed on white cloth prevents the fixation of albumen colours, though in this connection it is not quite so convenient to use as zinc sulphate, which is both cheap and effective. Mixed with steam Alizarin red, nitrate of ammonia enables it to resist albumen colour cover patterns, and thus to produce a clean-cut red on a fancy ground not specially engraved for it. This latter style is not much used at present.

(6) **Chrome Yellow and Orange Pigments.**—These pigment colours, although usually bought, are made quite as well and much more cheaply by the colour mixer himself.

CHROME YELLOW I. (Maize).

a { 760 grms. acetate of lead
  4000 ,, boiling water.

Add gradually—

b { 300 grms. bichromate of potash.
  3000 ,, boiling water.

Wash four times by decantation and filter to a stiff paste

CHROME YELLOW II. (Lemon).

a { 500 grms. lead acetate.
  5000 ,, water.

Dissolve, cool, and add, whilst stirring, a cold solution of-

b { 90 grms. bichromate of soda.
  115 ,, aluminium sulphate.
  2000 ,, water.
  35 ,, sulphuric acid 168° Tw.

Both solutions must be cold, otherwise the pigment tends to become reddish, more like the maize shade. Wash and filter as above.

CHROME ORANGE.

a { 600 grms. acetate of lead.
  4000 ,, water (boiling).

b { 120 ,, bichromate of potash or soda.
  1000 ,, water.
  1440 ,, caustic soda 15° Tw.

Add *b* to *a* slowly, stirring constantly, then stir half an hour, wash five times by decantation, and filter to 1150 grammes.

The above three pigments are used for coloured discharges on Indigo, Aniline black, basic, and Alizarin colours, and also for ordinary steam work on white grounds. They are thickened with gum tragacanth, and fixed by means of albumen or its substitutes.

(7) **Prussian Blue Pigment.**—Prussian blue is an important element in the discharging of Turkey-red by the acid process, and it is also used largely in the chromic acid discharge of dyed Indigo for the production of greens and light blues. A practical recipe for its manufacture is as under :—

PRUSSIAN BLUE PIGMENT I.

a { 1000 grms. copperas ($FeSO_4.7H_2O$).
  5000 ,, water.

b { 1000 ,, yellow prussiate of potash.
  5000 ,, water.

Add *b* to *a*, stir well, and oxidise the white precipitate by adding gradually first—

1060 grms. hydrochloric acid 28° Tw., and second—
1800 ,, bleaching powder solution 12° Tw.

Allow to settle, and then wash well three times by decantation with boiling water. Settle, and filter through a closely-woven woollen cloth until the paste weighs about 2700 grammes = 25 per cent. paste.

A light blue lake is obtained by grinding together in a mill—

750 grms. China clay.
350 ,, gum tragacanth thickening.
250 ,, Prussian blue, prepared as above.

The oxidising of the white precipitate ($Fe_2Fe(CN)_6$) is perhaps better performed with soda chemick, so as to avoid the formation of calcium sulphate.

The precipitation of this salt can also be avoided by washing before oxidising, but, except in rare cases, its presence is not objectionable, besides which a great part of it is dissolved by the wash-waters.

Another but more expensive method of making a Prussian blue free from calcium sulphate is the following:—

Prussian Blue II.

$a\begin{cases} 1{,}310 \text{ grms. copperas.} \\ 10{,}000 \quad ,, \quad \text{water.} \end{cases}$

$b\begin{cases} 1{,}000 \quad ,, \quad \text{yellow prussiate of potash.} \\ 10{,}000 \quad ,, \quad \text{water.} \end{cases}$

Add together *a* and *b*, settle, decant supernatant liquor, and oxidise with—

75 grms. nitric acid 66° Tw.
200 ,, warm water.

Wash well by decantation and filter to 2700 grammes=25 per cent. Prussian blue.

(8) **Soda Chemick** 8° Tw.—This is simply hypochlorite of soda, prepared by the double decomposition of sodium carbonate and bleaching powder. It is useful in some classes of bleaching, for clearing printed fabrics, and as an addition to soap solutions employed for soaping Paranitraniline reds, etc.

Soda Chemick 8° Tw.

1000 c.c. bleaching powder solution 9° Tw.= 30 grms. of available chlorine.

Add—

$\begin{cases} 61 \text{ grms. soda ash.} \\ 258 \quad ,, \quad \text{water.} \end{cases}$

Allow the calcium carbonate to settle and use the clear liquor.

(15) Soap.

Soaping is one of the most important of the after-treatments to which nearly all printed goods are subjected. The soap used must be neutral, or at most contain only a trace of free alkali, otherwise the colours are apt to be injuriously affected. Some colours, like Aniline black, Vat colours, and the insoluble Azo colours, are not harmed by a little free alkali, but by far the greater number of steam and dyed colours are more or less soluble in alkaline solutions, and therefore it is always safer for the standard soap used in any works to be as neutral as it is possible to make it. Any extra alkali can be added when required for special purposes.

Apart from their use as cleansing agents, soaps are sometimes used to facilitate the dyeing of direct colouring matters, as additions to thickenings, prepares, and finishes, to increase their softness, and, less frequently, as fixing agents for a limited class of mordants like oleate of lead, which is used as a mordant for the Phthaleïn family of colouring matters.

The easiest and quickest method of making soap is to boil oleïc acid with a calculated amount of caustic soda. The operation only takes an hour, and the resulting soap is a practically pure oleate of soda, suitable for all purposes.

50 per cent. Soap.

50 kilos. oleïc acid.
43 ,, caustic soda 36° Tw.
7 ,, water.
———
100

Boil for one hour, then test in the usual way for neutrality, and add more acid or a little more soda according to circumstances: after each correction boil up again. When satisfactory, add water to replace that evaporated, and make the whole up to 100 kilogrammes = 50 per cent. fatty acid.

In England most of the soaps used in calico printing are made from cotton-seed or palm oils. An example of each of these, as made on the large scale, is given below.

Cotton-Seed Oil Soap.

1200 litres *cotton-seed oil* are placed in a large jacketed pan and heated.
1800 ,, *caustic soda* 17½° Tw. are then added in portions of 500 litres, and the whole is boiled 10–12 hours until the oil is completely saponified. Any excess of oil or soda is corrected by a suitable addition of one or the other, and after re-boiling, the soap is run out of the pan into forty-gallon casks, in which it sets as a stiff jelly, containing roughly 40 per cent. of soap. The glycerin is allowed to remain in the soap, as it has no effect on the goods; besides which, its separation would only prolong the process without any corresponding advantage accruing. If required for sale, the soap can easily be freed from glycerin by salting out; but if required for use in the works, the cost of carriage of a useless ingredient (glycerin) does not enter into the question, and can be ignored.

In palm-oil soap it is usual to eliminate the glycerin, with doubtful gain.

Palm-Oil Soap.

50 kilos. bleached palm oil.
100 ,, water.
Heat to the boil and add—
30 kilos. caustic soda 70° Tw.

Boil 10–15 hrs. Then salt out with 20–25 kilos. of common salt added to the above mixture, stir up well, and allow the soap to set on the surface. Then run off the salt solution which contains the glycerin, add 150 kilos. of water, boil up again, and salt out a second time. When the second salt solution is drawn off, boil the soap again, then run it into flat zinc-lined boxes, and allow it to set hard, after which it is ready for use. The saponification must be complete before any salting out is attempted; and it is well, also, to ensure that the soap is more or less neutral, although a good deal of the free alkali is carried off by the saline wash waters. In the last boiling of the soap, after the second salting out, sufficient water is added to reduce the soap to a strength corresponding to 60 per cent. *fatty acid.*

The strength of the soap solutions used varies with the class of work under treatment. Turkey-reds and other Alizarin-dyed goods, such as chocolates and purples, will stand a prolonged treatment in a boiling 2–3 per cent. soap solution, while some of the more delicate kinds of steam work only require a moderately hot solution containing $\frac{1}{10}$ to $\frac{1}{2}$ per cent. of soap. Between these extreme limits all percentages of soap are employed, and the temperature is likewise determined by the known resistance of the colours to hot soap solutions.

(16) Thickening Pastes.

The following thickening pastes are in general use, and, apart from unimportant modifications, represent those employed throughout the whole calico-printing industry. In many cases two or more thickenings may be mixed together, or a mixed thickening may be boiled at one operation: these

points, however, are matters of experience, and cannot either be generalised or dealt with apart from the circumstances which govern them.

The following thickenings may be used both for making standard colours and for diluting (technically: reducing) the same.

I. Starch Paste 15 per cent.

1,500	grms.	wheat starch.
8,100	,,	water.
400	,,	cotton-seed oil.
10,000		

Boil and cool.

II. Acid Starch Paste 20 per cent.

2,000	grms.	wheat starch.
5,500	,,	water.
2,200	,,	acetic acid 9° Tw.
300	,,	cotton-seed oil.
10,000		

Boil and cool.

Very useful for dark basic colours and such as require acetic acid for their solution.

III. Starch Tragacanth Paste.

1000	grms.	wheat starch.
3000	,,	water.

Mix in the cold and add—

6000 grms. tragacanth thickening 6 per cent.

Boil and cool.

For thickening diazo solutions, and, when thinned down, a suitable thickening for medium blotches.

IV. Acid Starch Tragacanth Paste.

1,200	grms.	wheat starch.
6,000	,,	water.
2,000	,,	6 per cent. tragacanth thickening.
800	,,	acetic acid 9° Tw.
10,000		

Boil and cool.

Used for reducing basic colours, and for general use where a soft acid paste is required.

V. Flour and Tragacanth Paste.—This paste is used for printing the Azoic colours, and also for reducing Madder colours—that is, the thickened solutions of aluminium and iron mordants. It possesses a good deal of body, and at the same time is soft, and penetrates better than most thickenings of the same consistency.

2,000	grms.	flour.
600	,,	acetic acid 9° Tw.
4,000	,,	water.
3,000	,,	tragacanth thickening 6 per cent.
300	,,	cotton-seed oil.
10,000		

Boil and cool.

VI. Alizarin Red Paste.

1,500	grms.	wheat starch.
7,000	,,	water.
700	,,	acetic acid 9° Tw.
500	,,	tragacanth thickening 6 per cent.
300	,,	cotton-seed oil.
10,000		

Boil and cool.

VII. Reducing Paste for Alizarin Pinks.

1,000	grms.	wheat starch.
7,100	,,	water.
500	,,	acetic acid 9° Tw.
1,000	,,	tragacanth thickening 6 per cent.
400	,,	cotton-seed oil.
10,000		

Boil and cool.

VIII. Gum Senegal Thickening 50 per cent.

5,000	grms.	gum Senegal.
5,000	,,	water.
10,000		

Allow to soak in the cold and then boil up. Take the solution out of the pan, filter it through calico into storage casks and there let it settle until all the sand and grit are deposited, when it is ready for use. Gum Senegal is the best thickening to use for light blotches when price is no object; it gives beautifully level shades, which possess a soft, delicate quality unapproached by any other kind of thickening, except, of course, the other natural gums—arabic, gedda, etc. The latter are prepared in precisely the same way as gum Senegal.

IX. British Gum Thickening.—The percentage of British gum used in a thickening varies with the degree of calcination. A moderately torrefied starch yields a good paste at 350 grms. per kilo.

350	grms.	British gum.
650	,,	water.
1000		

Boil and cool.

If the gum is acid it must not be boiled. British gum is used, in place of the more expensive Senegal, for all kinds of discharges, blotches, etc.

X. Tragacanth Thickening 6 per cent.

600	grms.	gum tragacanth.
9,400	,,	cold water.
10,000		

Allow to soak 24–30 hours, and then boil until the mucilage becomes quite smooth.

Used in combination with other thickenings, and also alone, for many colours which are required to penetrate well into the fabric.

XI. Alkaline Thickening.—Used for Indigo, Sulphur colours, most vat colours, and for the discharging of tannin-mordanted goods.

1,500 grms. British gum.
8,500 „ caustic soda 77° Tw.

10,000

Mix in the cold and then heat to 140° F.

XII. Albumen Solution 50 per cent.

1000 grms. egg albumen.
1000 „ water (cold).

2000

Dissolve in the cold.

Blood albumen is usually made as 40 per cent. solution. Both are employed for fixing pigment colours.

XIII. Paste for reducing Acid Resists.

$\left\{\begin{array}{l}\text{1,000 grms. China clay.}\\ \text{1,000 „ water.}\end{array}\right.$

Grind to a fine smooth paste and add—

2,500 grms. British gum.
5,500 „ water.

10,000

Boil and cool.

XIV. Karaya Gum Thickening 20 per cent.

$\left\{\begin{array}{l}\text{200 kilos. Karaya Gum (finely ground).}\\ \text{500 „ water.}\end{array}\right.$

Mix well and add gradually—

$\left\{\begin{array}{l}\text{0·600 kilo. sodium peroxide.}\\ \text{125 kilos. water.}\end{array}\right.$

Stir 1 hour in the cold and then add a further

$\left\{\begin{array}{l}\text{0·650 kilo. sodium peroxide.}\\ \text{75 kilos. water.}\end{array}\right.$

Stir ½ hour; raise temperature to boil and boil for 3½ hours; cool and neutralise with HCl 30° Tw., and make up to

1000 litres.

If boiled under pressure, in an autoclave, Karaya gum dissolves much more quickly than in an open pan, and requires neither grinding nor the addition of sodium peroxide to bring about its solution. The solution obtained in this way is darker and more irregular in viscosity than that given by the recipe above, but when bleached with hypochlorite it is very suitable for finishing purposes. For printing colours the open-pan method is preferable.

Karaya gum is an efficient substitute for gum Senegal in many styles. Its chief applications are in the printing of blotches, discharges, reserves, and flannelettes.

The fourteen preceding pastes or thickenings include all that may be considered as standards. Other mixtures may be made as required, and the various proportions and ingredients modified as occasion dictates.

Choice of Thickenings.—The choice of the particular thickening to employ in a given case is largely a matter of experience, and depends upon many factors. The quality, style, and condition of the engraving must be taken into consideration, the cost of production must be kept in mind, the question as to whether or

not the colour is to penetrate to the back of the fabric must be considered, the surface of the cloth must also be allowed for, and the sharpness or otherwise of the impression must be taken into account. No less important than these points is the question of the finish which has to be put on the printed goods. If they are required to possess a soft feel, the thickening of the printing colour must be capable of being entirely removed without subjecting the goods to a treatment of such severity as to injure the colours; in other words, the thickening must be easily soluble in warm solutions, and not require too prolonged a treatment for its elimination. For this purpose gum Senegal, gum tragacanth, and British gum are the best thickenings to use. On the other hand, when the goods are required to possess a stiff, boardy feel, starch may be used with advantage if it fulfils the other conditions essential to a good print, namely, evenness and delicacy. Again, coarse engraving requires much thicker colour to produce a similar impression to that obtained from delicate shallow engraving; but, on the contrary, a thicker colour may be used for lightly engraved blotches or backgrounds than is demanded by coarse, heavy blotches. A thick colour used for these latter would in most cases display every line of the engraving, whereas a thin colour would spread out by capillary attraction, and thus produce a more even ground. The colours employed for two stippled rollers, falling one over the other, may be thickened with starch or gum Senegal, according as the stipple is required to show distinctly or to gradate imperceptibly. Sometimes the darker colour is thickened with starch and the lighter with gum Senegal, in which case the gradation is distinct, but not too hard.

The best thickening for yielding even blotches is undoubtedly gum Senegal (or gum arabic), but it cannot be used for dark colours on account of the fact that colours thickened with it wash out a good deal on soaping, and, if strong, tend to soil the other parts of the pattern and the white ground of the cloth. For dark blotches, therefore, tragacanth, or tragacanth mixed with starch, are the thickenings most commonly employed; and when the blotch is engraved in fine scale, starch alone is often a most suitable thickening agent to use, since it is cheap and economises colouring matter. A colour thickened with gum Senegal, or even British gum, only yields about half the depth of shade of one of the same strength thickened with starch; hence starch should always be used wherever possible. Strongly alkaline and strongly acid colours are, as a rule, thickened with either natural or artificial gums, as they act on starchy or farinaceous bodies, and either thicken them unduly and make them sticky, or decompose them altogether.

Another point to notice is that the same colour does not give the same shade with different thickenings. For instance, a colour composed of Alizarin orange, Alizarin yellow, Alizarin blue, and acetate of chromium (a fawn colour) produces reddish shades with starch, and much yellower and softer shades with tragacanth thickening; so that, irrespective of depth, the tone of a colour is also influenced by its thickening, and consequently thickenings are not interchangeable without some alteration in the proportions of the constituents of a mixture of two or more colours.

The order in which the colours of a multicolour pattern are worked in the printing machine further influences the choice of thickening in many cases; notably in those of delicate, easily soiled, and sensitive colours like pinks, salmons, and terra-cottas, fawns, drabs, and pale blues. In such cases it is always advisable to thicken them with gum of some sort, since the scum (from the following rollers) on the surface of a gum colour washes off much more easily (and produces less soiling) than it would, or does, from the surface of a starch colour.

Broadly speaking, the thickening agents given below will, in general, be found the most suitable for the following styles of work :—

(*a*) Blotches or Backgrounds.—Pale: gum Senegal or gum arabic, Karaya gum, and also British gum. Dark: gum tragacanth alone, or a mixture of tragacanth and starch. When starch alone is used, it mostly requires flattening or distributing evenly by passing under a "starch roller," *i.e.* an unengraved roller, working in water or starch paste, and furnished with doctors as usual.

(*b*) Fine, Sharp Impressions.—Thick colour of any thickening chosen. Starch and the gums are the best; gum tragacanth the least desirable.

(*c*) Stippled Work.—For crisp impressions and sharply defined shadow, use thick colour; for obtaining delicate imperceptible gradation, use thin gum Senegal for preference, and in the second place thin tragacanth or British gum.

(*d*) Where the colour is required to penetrate to the back of the cloth, gum tragacanth is one of the best thickenings to use; and after that, tapioca starch, wheat starch, and flour, all used as thin as possible.

(*e*) Acid Resists, Discharges, and Colours.—Gum Senegal, Karaya gum, or British gum, either with or without China clay. Starch may also be used in many instances.

(*f*) Alkaline Colours, Resists, and Discharges.—Gum Senegal, British gum, and sometimes maize starch.

(*g*) Madder Style.—Flour and starch, singly or mixed together. Flour is especially good for thickening iron and aluminium acetates, though, as a rule, it is mixed with a little starch for this purpose. British gum is also used for light madder blotches and pads.

(*h*) Pigment Colours.—Albumen and tragacanth; more rarely albumen and wheat starch.

(*i*) Soft Goods, Flannelettes, Sateens, etc.—Gum Senegal, Karaya gum, or gum tragacanth are the best to use wherever they can be afforded, especially if the pattern contains heavy masses of solid colour. Small masses and outlines are better and more economically printed in a starch-thickened colour. British gum or dextrin is also a good thickening for blotches in these classes of work, and is usually substituted for the high-priced Senegal. British gum yields yellower shades of Alizarin pink than gum Senegal.

These remarks must not be taken as constituting hard-and-fast rules for the application of particular thickening matters, but rather as indicating, in a slight degree, some of the purposes to which they are peculiarly adapted. It often happens that the printing price of goods is too low to allow of their being executed in the best way, and in such cases the thickening is generally the first item to be cut down, so that, as previously stated, the choice of a thickening is governed by considerations other than its peculiar appropriateness to the work in hand.

OXIDISING AND REDUCING AGENTS.

Both oxidising and reducing agents play such an important part in textile printing that, although they are dealt with to some extent in an elementary course in chemistry, it has been thought advisable to classify them under one heading, and to enumerate and briefly describe those which are specially applied in printing.

Oxidising Agents.

The simplest and most universal oxidising agent is naturally *atmospheric oxygen.* The printer employs this for obtaining various results, such as the

oxidation of iron mordant in ageing, the discharge of tannic acid, the development of Indigo and other vat colours on the fibre, etc. The oxidising action of the air is strongly influenced by various conditions, *e.g.* whether the oxidation takes place in a neutral, acid, or alkaline medium, and whether with or without the assistance of such agencies as heat, moisture, and sunlight. In an acid or neutral medium, air oxidation is usually slow or does not take place. An example of slow oxidation in an acid medium is the ageing of calico impregnated with ferrous acetate (black liquor). In presence of alkalies, especially caustic alkalies, air oxidation usually proceeds much more rapidly. Thus in neutral or acid solution, tannic acid does not undergo oxidation when exposed to the air, but in presence of caustic soda it is very rapidly oxidised and destroyed. Similarly, Indigo and other vat colours are all exposed to the air after dyeing or printing and reducing in the alkaline condition, when oxidation takes place rapidly and evenly. If they were acidulated after dyeing or steaming, oxidation would indeed take place, but it would be very slow. As in all chemical changes, heat generally accelerates oxidation. Direct sunlight and ultra-violet light also seem to promote air oxidation, but no use is made of this in textile printing. The presence of moisture is in most cases indispensable to oxidation. Thus indigo white, if perfectly dry, can be exposed to a dry atmosphere without turning blue, and hydrosulphite of soda, one of the most oxidisible bodies, can be kept in dry air indefinitely. As is well known, catalysts often favour air oxidation, but they do not find employment for this purpose in calico printing. A notable exception to this is met with in Green's Aniline black process, in which paraphenylene diamine brings about the oxidation of aniline to Aniline black by atmospheric oxygen alone.

In some cases of air oxidation it has been noticed that the amount of oxygen consumed is considerably in excess (often double) of that required by theory. Thus, Herzog and Manchot found that if the barium compound of indigo white is oxidised in the air, it yields Indigo blue and an equivalent amount of hydrogen peroxide. The reaction might be expressed by the equation

$$C_{16}H_{12}N_2O_2 + O_2 = C_{16}H_{10}N_2O_2 + H_2O_2.$$

It is assumed that, under such conditions, the oxygen molecule is split into two atoms of nascent oxygen, the reaction resulting in the simultaneous formation of Indigo and hydrogen peroxide. This constitutes one of the best examples of what is called "auto-oxidation." In how far this phenomenon plays a part in textile colouring is not known with any degree of certainty, but it is possible that it may account for some things which have hitherto remained unexplained. (See R. E. Crowther, *J. S. D. and C.*, 1911, p. 146.)

Ozone, which is technically produced by the action of the silent electrical discharge on dry air, has been suggested as a means of bleaching, but has not met with practical success.

Since oxygen is more readily soluble in water than nitrogen, it follows that the air dissolved in water is richer in oxygen than the atmosphere. Ordinary water must therefore be considered in a sense as an oxidising agent: when saturated with air at atmospheric pressure it contains at the ordinary temperature about 6 c.c. of dissolved oxygen per litre.

Hydrogen Peroxide (H_2O_2), which comes into the market as a 3 per cent. solution, and which is sometimes prepared by the user by adding sodium peroxide to cold dilute sulphuric acid, does not lend itself to any of the processes of printing, but is largely used for bleaching delaines previous to their being printed.

Sodium Peroxide (Na_2O_2) comes into the market as a cream-coloured powder. Added to a small quantity of water it liberates much heat and

oxygen is evolved in large amount. If any oxidisable matter is present under these conditions it will probably take fire spontaneously and burn fiercely. For dissolving sodium peroxide it is recommended to add it to about six times its weight of broken ice.

Chlorine in the free state was the first artificial bleaching agent employed for cotton. It was soon abandoned in favour of Eau de Javelle, this being subsequently replaced by bleaching powder. Within recent years liquefied chlorine has come into the market, and is sold in steel cylinders, from which the gas can be continuously drawn on opening the tap. Endeavours have been made to re-introduce gaseous chlorine for the bleaching of calico and to utilise it for the chlorination of delaines, but they have not met with much success.

In water, chlorine dissolves at the ordinary temperature to the extent of 2·4 vols. to one of water. The aqueous solution is most conveniently prepared by adding hydrochloric acid to a solution of bleaching powder or of hypochlorite of soda. Both in bleaching and in the chlorination of wool chlorine acts as an oxidising agent.

Bleaching Powder, technically the most important of the hypochlorites, is prepared by absorbing chlorine in slaked lime, and is generally assumed to consist of a mixture of calcium hypochlorite and calcium chloride, although it never contains the amount of available chlorine demanded by the formula $Ca(OCl)_2 + CaCl_2 + 2H_2O$. This should be 49 per cent., but a good bleaching powder seldom contains more than 35 per cent. of available chlorine. Bleaching powder always shows an alkaline reaction, this being due either to the presence of free lime or basic hypochlorites. Bleaching liquor, obtained by dissolving chlorine in milk of lime, comes into the market as a clear liquid, generally standing at 28° Tw., and containing, like bleaching powder, calcium hypochlorite as its effective constituent. By hydrochloric acid, calcium hypochlorite, like other hypochlorites, is decomposed with evolution of chlorine. The chief use of bleaching powder is in bleaching, but smaller quantities are also used for clearing whites, the discharge of Turkey-red and other purposes.

Hypochlorite of Soda is made by dissolving chlorine in caustic soda, or by the action of sodium carbonate on bleaching powder, or, lastly, by the electrolysis of brine. It is used to a limited extent in bleaching and in chlorinating wool.

Chlorate of Soda ($NaClO_3$) now comes into the market in an almost pure condition, and, in consequence of its being cheaper and much more soluble in water, has almost entirely replaced *chlorate of potash* as an oxidising agent in the tinctorial industries.

Chlorate of soda comes into the market in the form of colourless crystals, and dissolves in its own weight of water at the ordinary temperature, and in half its weight at the boil. When used alone in a neutral or slightly alkaline solution, it can scarcely be regarded as an oxidising agent; but in presence of mineral acids, and more especially of catalysts like vanadium chloride, cerium chloride, yellow prussiate, salts of copper, etc., it acts as a powerful oxidising agent, and is extensively employed as such in the production of Aniline black and in discharge work.

Barium Chlorate [$Ba(ClO_3)_2$] forms colourless crystals, which are soluble in water. It is not used as such in printing, but serves for the production of other chlorates, such as chlorate of alumina and aniline chlorate, by double decomposition with the corresponding sulphates.

Chromic Acid (CrO_3), although commercially available, is too drastic an oxidising agent to find employment in textile printing. Its salts, however, the chromates and bichromates, are extensively used.

Bichromate of Potash ($K_2Cr_2O_7$) crystallises in hard, well-defined orange crystals and is not very readily soluble in water, the solution saturated at the ordinary temperature containing about 9 per cent. of the salt. As such it does not usually exert an oxidising action, though this may occur under certain conditions. Thus, if calico is impregnated with a solution of bichromate of potash and is then exposed to sunlight or to ultra-violet light, the fabric is tendered through formation of oxycellulose, and a considerable amount of chromic oxide is precipitated on the fibres. Mineral acids, like sulphuric acid, liberate chromic acid from bichromate of potash.

$$K_2Cr_2O_7 + H_2SO_4 = 2CrO_3 + K_2SO_4 + H_2O.$$

Chromate of Potash (K_2CrO_4) is easily obtained from the bichromate by neutralising with potash or caustic potash.

$$K_2Cr_2O_7 + 2KOH = 2K_2CrO_4 + H_2O.$$

Chromate of potash forms yellow crystals, which are much more soluble in water than the bichromate. In itself it is not an oxidising agent, but acts as such in presence of acids, such as sulphuric acid, because they liberate chromic acid from it.

Bichromate of Soda ($Na_2Cr_2O_7 + 2H_2O$) is much more readily soluble in water, and is also cheaper than bichromate of potash, and for these reasons it has almost entirely taken the place of the latter in textile colouring. It forms orange-coloured deliquescent crystals, which dissolve in their own weight of water at the ordinary temperature. In other respects it resembles the potassium salt.

Chromate of Soda ($Na_2CrO_4 + 10H_2O$) is obtained by neutralising the bichromate with soda or caustic soda.

The chromates and bichromates find extensive application in the fixation of Aniline black and in Indigo discharge work.

Red Prussiate of Potash [$K_3Fe(CN)_6$] comes into the market in the form of orange-red crystals. It is fairly soluble in water, and acts in presence of caustic alkalies as a powerful oxidising agent.

Permanganate of Potash ($KMnO_4$).—A deep purple salt, possessing powerful oxidising properties in either acid or alkaline solution. It is occasionally used in the bleaching of cotton, in the eradication of printing faults, in the discharging of colour from spoilt goods, and in the production of Manganese brown. It cannot be employed in printing, since its oxidising action is so energetic that it destroys all thickening agents except silicate of soda, and silicate of soda is an impracticable thickening for many reasons.

Permanganate of Potash, $KMnO_4$, is sold in the form of dark violet needle-shaped crystals, which dissolve in water with an intense bluish-red colour. Permanganate of potash is one of the most powerful oxidising agents, and acts as such in neutral, alkaline, and acid solution. When acting in neutral solution it deposits hydrated peroxide of manganese, and simultaneously liberates caustic potash.

$$2KMnO_4 + 3H_2O = 2KOH + 2MnO(OH)_2 + 3O.$$

It is a good bleaching agent for cotton and linen, and finds some application as such. According to H. Kämmerer (Eng. Pat. No. 5612, 1907), it may be used for preparing wool for printing by running the material through a 10 per cent. solution of sulphuric acid containing a small amount of permanganate. The process has several advantages over the usual chlorinating process.

The other well-known oxidising agents are only of very small importance in

textile printing. Thus, **sodium nitrate** has been more or less successfully employed for Indigo discharge work according to Freiberger's process.

Bromate of Soda has been suggested for the same purpose.

Persulphates and **perborates** have also been suggested as oxidising agents for various purposes, and they find occasional application for the development of printed vat colours. The same applies to **peroxide of lead** (PbO_2) and **peroxide of manganese** (MnO_2). **Ferric** and **cupric salts** may be regarded as mild oxidising agents; and although copper compounds find extensive application in textile colouring, they are usually regarded more in the light of carriers of oxygen than of oxidising agents.

Reducing Agents.

Broadly speaking, reducing agents may be defined as substances which more or less readily withdraw combined oxygen from or add hydrogen to other substances. They generally consist either of elementary bodies like zinc and other metals in a fine state of division (also metalloids like red phosphorus), or of lower oxides or compounds of lower oxides of the elements which readily pass into a higher state of oxidation.

In textile printing, reducing agents find application for several different purposes. Thus they may be used for reducing metallic oxides, such as ferric oxide, to prevent local fixation of the iron, or of chromic acid, as in certain processes of mordanting cotton with chromium, or, again, for the discharge of Manganese bronze. Another use is for reducing Indigo and other vat dyes to their alkali-soluble leuco compounds, and in this capacity they find employment in dyeing, in direct printing, and in discharge work. Their action on azo dyes is of a different character, inasmuch as these are completely destroyed when reduced, and the colour does not consequently return on exposure to the air. The rupture of the molecule invariably takes place in the azo group. Thus, in the case of Alphanaphthylamine claret, the reduction takes place according to the equation

$$C_{10}H_7N:N.C_{10}H_6OH + 2H_2 = C_{10}H_7NH_2 + C_{10}H_6\begin{cases}OH\\NH_2\end{cases},$$

alphanaphthylamine and amidonaphthol resulting.

In case the azo dye contains two azo groups, it is evident that it will require twice the amount of reducing agent; and if it contains a nitro group, the amount required is still further increased. Thus, in discharging Paranitraniline red, according to the equation

$$C_6H_4\begin{cases}NO_2\\N:N.C_{10}H_6OH\end{cases} + 5H_2 = C_6H_4\begin{cases}NH_2\\NH_2\end{cases} + C_{10}H_6\begin{cases}OH\\NH_2\end{cases} + 2H_2O.$$

Not all azo dyes are reduced with the same facility. Thus, most of the direct cotton colours are easily discharged by reducing agents, while the insoluble Azoic dyes are much more difficult to discharge. With mixtures of azo dyes, selective action is sometimes noticed. A typical case of this kind may be observed in the green produced by dyeing cotton with a mixture of Chrysophenine and Diamine sky blue. If this is treated with stannous chloride, the blue only is discharged, leaving the yellow intact; but if titanous chloride be applied in limited amount, the yellow only is discharged; with excess of the latter reagent, the whole of the colour is discharged.

In some cases a leuco compound of a colouring matter may serve for the reduction of another colouring matter. Thus, according to Eng. Pat. No. 21746, 1905, the alkaline solution of Indigo white, if allowed to act upon Brom-indigo,

reduces the latter to its alkali-soluble leuco compound, Indigo being precipitated. Advantage is taken of this behaviour of the leuco compounds of certain dyestuffs, such as Patent blue, Erioglaucine and Induline scarlet, in order to accentuate the discharging action of hydrosulphite (sulphoxylates). The amount of dyestuff required in the discharge paste is very small in comparison with the hydrosulphite present, so that the former appears to act in a sense as a "carrier of hydrogen." Still better results are obtained by substituting *anthraquinone* for these colouring matters. This substance is readily reduced by the hydrosulphite to the corresponding hydroanthraquinone, and this in turn reduces the dyestuff, being reconverted thereby into anthraquinone, the cycle of reactions continuing until the reduction is complete.

Another important function of reducing agents in textile printing is based upon their action on diazo compounds, which are reduced thereby to the corresponding hydrazines, which latter do not react with phenols to form dyestuffs. Thus, when stannous chloride is allowed to act on nitro-diazobenzene chloride (diazotised paranitraniline), reduction takes place in the following sense:

$$C_6H_4\begin{cases}NO_2\\N:NCl\end{cases} + 2H_2 = \begin{array}{l}N\begin{cases}C_6H_4NO_2\\H\end{cases}\\|\\NH_2.HCl.\end{array}$$

This type of reduction is utilised in the production of the resist style in the application of insoluble Azoic dyes (*q.v.*). Although this is the accepted view, it is found (P. P. Thompson, *J. S. D. and C.*, 1921, p. 10) that under certain conditions half the amount of reducing agent of that required by the above equation will cause the cessation of the reaction with a phenol. This is due to the formation of an insoluble diazo hydrazide.

Zinc Dust, or zinc powder, is the product which distils over from the retorts in the extraction of the metal from its ores. It forms a fine, heavy, slate-coloured powder, which consists of a mixture of metallic zinc and oxide of zinc. A good product should contain about 80 per cent. of metallic zinc. Exposed to a damp atmosphere, zinc powder is liable to deteriorate rapidly, oxidation taking place.

Although zinc powder constitutes one of the most powerful reducing agents, it finds practically no direct application in printing, partly on account of its tendency to stick in the engraving of the printing rollers, and partly because of the grit which it contains. On the other hand, it is the chief reducing agent employed in the dyeing of Indigo and certain other vat dyes, and also serves as the reducing agent in the manufacture of hydrosulphites. When acting in its capacity of reducing agent, zinc passes directly to the condition of zinc oxide, ZnO, no intermediate lower oxide being known.

Stannous Chloride ($SnCl_2.2H_2O$), technically known as "Tin crystals," forms well-defined colourless crystals, and usually comes into the market in hermetically sealed iron drums. It is a fairly strong reducing agent, and was formerly used in large quantities in calico and wool printing for discharging azo dyes, and in calico printing as a resist under insoluble Azoic dyes. At the present time it has been to a large extent replaced by cheaper and more efficient reducing agents. The aqueous solutions of stannous chloride show a tendency to hydrolyse, with formation of free hydrochloric acid, which may bring about the tendering of cotton. To obviate this defect, sodium acetate or ammonium sulphocyanide is usually added to printing pastes containing stannous chloride.

Titanous Chloride ($TiCl_3$) comes into the market in the form of a dark violet 20 per cent. solution. It is one of the most powerful acid reducing agents

known, but has not hitherto been successfully applied in calico printing on account of its acidity, which causes tendering on drying or steaming. In dilute aqueous solution this defect does not occur; and in consequence of the rapidity and completeness with which it reduces azo dyes, titanous chloride is the most suitable reagent for stripping these colours, *e.g.* in spoilt work. To prevent the precipitation on the fibre, in such cases, of titanic hydrate, some oxalic acid should be added to the stripping bath. **Titanous sulphate** [$Ti_2(SO_4)_3$] is also a commercial article in a 20 per cent. solution, and is used, like the chloride, for stripping purposes.

Titanous Sulphocyanide [$Ti(CNS)_3$] obtained by double decomposition of titanous sulphate and barium sulphocyanide, while being as energetic a reducing agent as the chloride, does not tender the cotton fibre, and can consequently be employed with good results in discharging of Direct colours, Azoic colours, and Indigo. In acting as a reducing agent in discharge work, it mordants the cotton in the discharged parts with titanic hydrate, so that the goods may be subsequently dyed, if desired, in any mordant colour, a coloured discharge being thus obtained. Thus, if calico dyed a medium shade of Indigo is printed with thickened titanous sulphocyanide, dried, and run through boiling caustic soda at 2° Tw., a white pattern on a blue ground results. If the piece is then dyed in Alizarin orange, a brilliant orange pattern on a blue ground is obtained. By printing simultaneously two colours on Indigo-dyed calico, one containing hydrosulphite N.F. (free from zinc), and the other titanous sulphocyanide, drying, steaming, running through boiling caustic soda, and then dyeing in Alizarin orange, both white and orange patterns are obtained on a blue ground.

Ferrous Sulphate or Copperas ($FeSO_4.7H_2O$) (see also p. 218) is not a powerful reducing agent in neutral or acid solution. When acted upon by caustic alkalies or milk of lime it is decomposed, yielding ferrous hydrate.

$$FeSO_4 + 2NaOH \rightarrow Fe(OH)_2 + Na_2SO_4,$$

which is a fairly strong reducing agent. Exposed to the air, it rapidly absorbs oxygen, with formation of ferric hydrate,

$$2Fe(OH)_2 + O + H_2O = 2Fe(OH)_3.$$

Ferrous sulphate was formerly used very largely for the "setting" of Indigo vats, but its use for this purpose is now very restricted, partly owing to the excessive amount of sediment found in the vat, and partly on account of the loss of Indigo (about 20 per cent.) which is experienced in dyeing in the "copperas vat." Small quantities of ferrous sulphate are used in the direct printing of Indanthrene (*q.v.*).

Sodium Hydrosulphite ($Na_2S_2O_4$).—According to Schär a solution of this salt was first prepared by Schönbein, who recognised its reducing properties. Schützenberger first prepared it in a solid state, and ascertained its composition to be $NaHSO_2$. The later researches of Bernthsen and others have shown, however, that its composition is represented by the formula $Na_2S_2O_4$.

Hydrosulphurous acid and its salts may be prepared in many different ways, but only one of these is used in practice, viz. the reduction of bisulphite of soda by means of zinc powder. Under the most favourable conditions the reaction takes place according to the following equation,

$$3Zn + 10NaHSO_3 = Zn_3Na_2S_3O_{10} + Na_2SO_3 + 3Na_2S_2O_4 + 5H_2O,$$

so that 65 parts of zinc should yield 174 parts solid hydrosulphite of soda.

A solution of hydrosulphite of soda is frequently prepared in the works for Indigo dyeing by adding zinc powder to commercial bisulphites of soda, in the

proportion of one pound of the former to one gallon of the latter, means being taken (*e.g.* addition of ice) to prevent undue heating. When the reaction is over, milk of lime is added in excess, and the product may then be used directly for dissolving Indigo, or as an addition to the vat. It is preferable, however, to filter the solution, *e.g.* through a filter press, but in doing so every care should be taken to prevent exposure of the liquid to the air, otherwise oxidation of the hydrosulphite may take place so rapidly that in a short time the solution loses its reducing power.

For some years past solid hydrosulphite of soda, containing amounts of $Na_2S_2O_4$ varying from 60 to 95 per cent., has been in the market in the form of a dry, almost white, powder. It is largely used in the dyeing of Indigo and other vat dyes, but, owing to the rapidity with which its solutions oxidise in contact with the air, it is not suitable for textile printing. When oxidised in the air hydrosulphite of soda yields bisulphite of soda.

$$Na_2S_2O_4 + H_2O + O = 2NaHSO_3.$$

Baumann, Thesmar, and Frossard discovered that when hydrosulphite of soda is treated with formaldehyde, it yields a compound which is stable in the air, but is decomposed on steaming, and then exerts a powerful reducing action. By their discovery the use of hydrosulphite in textile printing was rendered practicable, with the result that many new and valuable effects have thereby been introduced which could not previously be obtained.

When concentrated aqueous solutions of hydrosulphite of soda and formaldehyde are mixed, an elevation of temperature takes place and a compound is formed having the composition $Na_2S_2O_4.2CH_2O.4H_2O$, and this product comes into the market under various names, such as **Hydrosulphite N.F., Hyraldite A.**

If the solution of this formaldehyde compound is subjected to fractional crystallisation it separates into two products, viz. the formaldehyde compound of bisulphite of soda and the formaldehyde compound of sulphoxylate of soda ($NaHSO_2$),

$$Na_2S_2O_4.2CH_2O + H_2O = NaHSO_3.CH_2O + NaHSO_2.CH_2O.$$

The pure sulphoxylate of soda has not been isolated. Its formaldehyde compound, when acting as a reducing agent, is converted into the formaldehyde compound of bisulphite of soda, and, as shown by the equation

$$NaHSO_2.CH_2O + O = NaHSO_3.CH_2O,$$

has twice the reducing capacity of ordinary hydrosulphite-formaldehyde.

The sodium sulphoxylate-formaldehyde compound ($NaHSO_2.CH_2O.2H_2O$) comes into the market under different names, such as **Rongalite C., Hydrosulphite N.F.** (conc.), **Hyraldite** (conc.), **Britulite, Formosul, Hydrosulphite A.F.C.,** in the form of irregular lumps which are white or colourless and semi-translucent. When kept for some time it gradually deteriorates and gives off a disagreeable smell. It is readily soluble in water, and the aqueous solution may even be boiled in contact with the air without losing its reducing action. When printed on calico or other material, dried and steamed (especially if the steam is superheated), it acts as a powerful reducing agent and does not tender the material.

Reductite is the name given to a compound of hydrosulphite of soda and glucose. It comes into the market in the form of a grey-coloured paste, and is used for the same purposes as the formaldehyde compound.

Alkaline sulphides, especially **sodium sulphide** (Na_2S), though cheap, and in many cases efficient as reducing agents, cannot be used in textile printing on account of their corrosive action on the copper rollers of the printing machine.

Sulphites and Bisulphites.—Of the sulphites, **potassium sulphite** (K_2SO_3) has been used in considerable quantities in resist work under insoluble Azoic dyes, on account of its great solubility in water. It comes into the market as a concentrated aqueous solution, standing at 90° Tw. Potassium sulphite, while acting as an efficient resist under Paranitraniline red, Alphanaphthylamine claret, etc., does not coagulate albumen, and can consequently be employed in conjunction with pigment colours for obtaining coloured resists. For white resists the cheaper **bisulphite of soda** ($NaHSO_3$) is largely employed at the present time. It comes into the market in solution, generally marking 62° Tw., or in the form of the solid metabisulphite ($Na_2S_2O_5$).

Arsenious Oxide (As_2O_3), generally known as "white arsenic," may be classed as a mild reducing agent. It is sold in the form of a fine white powder, and finds a limited application as a reducing agent in preventing the fixation of iron. **Arsenic trisulphide** (As_2S_3) was formerly used as a reducing agent for Indigo.

Of other inorganic substances, **Hydrazine sulphate** ($N_2H_4.H_2SO_4$) may be mentioned as having been suggested as a means for discharging direct cotton colours; but although it is now technically available, it is doubtful whether it finds any application in textile printing.

Glucose ($C_6H_{12}O_6$) is prepared by hydrolysing starch by heating under pressure with dilute sulphuric acid. The acid is subsequently neutralised and removed by means of milk of lime. Glucose comes into the market in the form of irregular lumps of a brownish colour, or in the form of a colourless transparent thick syrup known as "crystal glucose." In either case the product does not consist of pure glucose, but contains, besides, many other organic compounds. In presence of caustic soda, glucose acts as a fairly powerful reducing agent, and is largely used in the direct printing of Indigo by the so-called "glucose" or "Schlieper and Baum" process. It also finds employment for the fixation of other vat dyes and of sulphide colours.

PART VII.

STYLES OF PRINTING.

STYLES OF PRINTING.

GENERAL.—Technically speaking, calico prints are not classified according to their styles of design, but according to their modes of production. What is meant, therefore, when a piece of print is described as belonging to a certain "style," is that it has been executed by a particular process, a process involving a series of chemical and mechanical operations more or less peculiar to itself. Some of these operations may (and sometimes do) individually form parts of other processes, but when certain of them are associated and performed in a definite order, they constitute a definite process and give rise to a definite style of printing. Hence calico prints are divided into distinct groups or styles according to the means whereby their colours are applied to and fixed upon the fibre.

This by no means implies that only one class of colouring matter can be used for a particular style. On the contrary, all colours that are capable of being applied and fixed in the same general way can be printed in combination so long as no one of them injuriously affects the others. Thus the various colours of an elaborate multicolour pattern, whilst perhaps bearing no resemblance to each other in chemical composition, are yet capable of being applied and treated in the same way, simply because each of them possesses certain properties which enable it to withstand the action of the various operations that are essential to the full development and fixation of each of the others. It must not be supposed from this that all colours belonging to a certain style of work can be printed together indiscriminately. Their powers of resistance to acids, alkalies, soap, etc., vary considerably, and must be taken into account when certain colours are used. For instance, pale shades of ultramarine blue printed along with strong Alizarin red and basic aniline colours are liable to be destroyed by the acid fumes given off by the red during steaming, or by the accidental acidity of the tartar emetic bath used for fixing the latter; and, again, Prussian blue printed in combination with the same colours is decomposed and converted into a buff by the hot, strong soap solution through which they are usually passed after steaming, fixing, and washing. In these and numerous other cases, when an unstable colour cannot be replaced, it is necessary to modify the process, and thus the main divisions or styles of calico printing are further subdivided into minor styles. Instances of this necessity for special treatment might be multiplied *ad libitum*, but the above will serve to show that sensitive colours cannot be employed in combination with those containing ingredients which are apt to act upon them detrimentally, even though both classes of colour may belong to the same general style.

To classify the styles of printing satisfactorily is a somewhat difficult matter, by reason of the fact that some of them will not readily take their place in any list, while others may be classed in several. On the whole, however, the following arrangement will be found convenient.

There are—

(1) DIRECT PRINTED STYLES, in which the colour is applied directly to the fibre by printing, and fixed thereon by steaming.

(2) DYED STYLES.—A mordant being first fixed upon the fibre, and the colour afterwards applied by dyeing.

(3) INSOLUBLE AZOIC COLOUR STYLES, depending on the production, by combination of diazo compounds with phenols, of the actual colouring matter on the fibre.

(4) DISCHARGE STYLES, in which a dyed ground or a mordant is removed locally, leaving a white or coloured pattern on the original ground.

(5) RESIST OR RESERVE STYLES, the object of which is to produce a pattern on a coloured ground by first printing on the white cloth a substance that will prevent the fixation of any colouring matter or mordant afterwards applied over it.

(6) RAISED STYLES.—Similar in many respects to the dyed styles, but produced with mineral bodies in place of dyestuffs, which are practically all organic bodies.

(7) LININGS.—A mixed style, made up of many others, but distinguished for the most part by the class of its patterns and colour effects.

(8) METAL PRINTING STYLES.—The application of metallic powders to the production of designs in gold, silver, etc.

(9) CREPONS OR "CRIMPS."—A style of work based upon the action of strong caustic soda on cotton, whereby crinkled stripe effects are obtained by printing on plain cloth.

And lastly, as belonging to no one style, those classes of work which are executed by a combination of parts of two or more styles, and cannot, therefore, be included in any, since they partake of the nature of several. Some combined styles are so generally employed as to constitute distinct classes. These will be dealt with as they occur in the consideration of the processes by which they are produced.

The above distinctions of styles are based upon the means and methods of applying colour to, and fixing it upon, the fibre, and as such they represent the general methods employed in the execution of all kinds of calico prints, be their ultimate use what it may. The textile colourist has nothing to do with the purpose to which a print is put beyond supplying suitable colours, and therefore the above technical arrangement of styles has been adopted in preference to that according to which goods are divided into cretonnes, dress goods, shirtings, etc.

Each of the foregoing styles may be divided into minor styles according to the class of colouring matter employed, but, in the main, the operations connected with these modifications remain the same, although the chemical reactions they bring about are different; so that all colouring matters that are capable of being applied and fixed in the same general way may be printed together, if they do not react upon one another in process.

(1) DIRECT PRINTED STYLES.

In direct printed styles the colour is applied to the fabric along with various substances which form an insoluble precipitate with it on steaming for a longer or shorter period. Amongst the most important colours applied in this way are those known as the Alizarin colours, basic colours, direct colours, Sulphide colours, vegetable colours, Aniline black, and certain mineral colours and pigments.

After printing, the goods are simply dried and then steamed, and, after a fixing process in the case of basic colours, soaped and washed.

The *direct style* might much more appropriately be called the *steam style*, since steaming is its most distinctive feature; but the term "steam style" has

unfortunately been applied, in some quarters, to a class of work distinguished by its defects—*e.g.* its gaudy colour, inharmonious combinations, general looseness to light and washing, and its utter lack of either technical or artistic merit —and consequently steam work has come to be looked upon by the public, or at least the untrained, as identical with the worst and cheapest of poor goods. So far from this being the case, however, some of the finest and the fastest colours known are fixed by steaming, and some of the highest class work produced is steam work.

The fastness of steam colours depends upon the colour lake being formed on the cloth itself; and in order to prevent any combination taking place between the various ingredients of a colour before printing, the mordants employed are only such as have no action on the colouring matter in the cold or in presence of certain substances added to further lessen their affinity for the colour base. In steaming, these restrainers are volatilised or decomposed, and, at the high temperature of the chamber, the mordants and colouring principles combine to produce an insoluble lake, which virtually dyes the cloth in just those parts printed. The colours developed by steam usually require several other operations to fix them thoroughly on the cloth; and the latter is also usually prepared in oleine, or some preparation of oleine and tin, for the purpose of both brightening the colours and rendering them faster to soap, etc.

The usual process followed in the production of the fast steam style consists in the following series of operations:—

(*a*) Preparing.—Pad the cloth in a $2\frac{1}{2}$–5 per cent. solution of castor oil oleine (soda or ammonia ricinoleate, with or without the addition of stannous or stannic salts). Dry.

(*b*) Printing.

(*c*) Steaming in continuous or cottage steamers.

(*d*) Fixing in $\frac{1}{2}$–2 per cent. solution of tartar emetic and chalk.

(*e*) Chroming (where required) in 1 per cent. solution of bichromate of soda.

(*f*) Soaping.—Steamed goods are always soaped to clear out all superfluous matters. The strength of the soap solution varies from $\frac{1}{10}$–$\frac{1}{2}$ per cent. of soap, and its temperature between 160° F. and the boil, according to the colours and effects required.

Fixing, chroming, soaping, and washing are all performed in the continuous open soaper already described. Where goods contain no basic colours, the fixing is omitted; and where Aniline black or Catechu or steam Prussian blue are absent, the chroming may likewise be dispensed with. Alizarin colours and other mordant colours require no other treatment after steaming than a simple washing and soaping. At the same time they are easily capable of withstanding the other operations, and can therefore be used in combination with practically every colour fixed by steaming.

Indigo and similar vat colours, Aniline black, and Paramine brown may also be included amongst the colours applied directly to the fibre by printing. They are not really steam colours in the ordinary sense of the term, neither can they be introduced into so great a variety of colour schemes as some of the "steam colours" proper; but steaming or ageing in a rapid ager is essential to their fixation; and in so far as they are applied and fixed by the same mechanical means as ordinary steam colours, they may, for convenience, be classed in one of the subdivisions of direct printing.

Application of Mordant Colours.

By mordant colours are understood those colouring matters which, while possessing no colouring power of any practical use in themselves, are yet

capable of combining with metallic oxides to form insoluble coloured precipitates on the cloth. They constitute one of the most important series of colours at the disposal of the calico printer; and if they do not yield the most brilliant shades, they at least possess qualities which compensate for this lack, and which render them of great value in the production of the highest class of decorative designs, and not less so in that of dress goods and strictly utilitarian fabrics.

As a class, the mordant colours are easily applied; they furnish a good range of rich, full colours, varying from bright reds, yellows, blues, and greens, to the softest and most delicate tones of grey, fawn, olive, and salmon; in direct printing any of them may be associated in almost any colour scheme, thus allowing of the designer's ideas being realised to the fullest extent, and affording the colourist ample scope in the arrangement of his colour combinations; and above all, they are of excellent fastness to light and soap.

Many of the *lakes* produced by the mordant colours are identical with those used by artists; and of the rest, the greater number are equally rich and permanent, so that an artist designer need have no fear of his work being crippled in reproduction if his design is drawn up, in the first instance, with due regard to the conditions of calico printing. Much of the outcry at modern colours is neither more nor less than an expression of ignorance; and if the self-satisfied critics would only condescend even to dabble in the subject they descant upon, they would soon learn to keep silence in the company of expert chemists and calico printers, who at least do know what they are using when they apply certain substances to cotton, linen, wool, or silk, and that is more than most "art critics" know when they attempt to belittle the results obtained by scientific research, and at the cost of much money, many failures, and long experience.

The mordant colour group includes both natural and synthetic dyestuffs, and its numerous members exhibit perhaps more diversity in chemical structure than those of any other group. The natural or vegetable colours, as prepared for printing, consist of extracts of various lichens, and of the leaves, barks, trunks, roots, flowers, and fruits or berries of a great number of shrubs, plants, and trees. The most important colours of this class, at present in use, are: Logwood, Catechu, Persian berries, Quercitron bark, Sapanwood, and Myrobalans. Others find occasional employment; but, for the most part, they have been displaced by their more permanent synthetic competitors.

Of the synthetic, or artificial, mordant colours the majority are derived from the Azo, Quinoneoxime, Oxazine, Oxyketone, Thiazol, Phthaleïn, and Anthraquinone groups, and they are met with in commerce under many names, a few of which, typical of the above classes, are as follows: Alizarin yellows G.G. and R., Diamond yellow; Resorcin green, Fast steam green, Nitrosine D.H.; Gallocyanine, Modern violet and blues, Chrome azurines, Gallazol green F.D.; Alizarin black S., Alizarin yellow C.; Galleïn, Cœruleïn; Alizarin, Alizarin orange, Alizarin blue; Chrome deep brown A.G., etc.

By the introduction of amino, methyl, ethyl, hydroxyl, sulphonic, and similar groups into the nuclei of the above parent compounds, and by other various and well-known means, it is possible to produce an almost infinite variety of new colours of an ever-increasing complexity of constitution.

The properties of colours are functions of their constitution, and the mordant colours are no exception to the rule; but, however much they differ in properties and constitution, their molecules are all possessed of one important feature in common, viz. that they contain one or more hydroxyl (or carboxyl) groups, to the presence of which is due their characteristic property of forming insoluble *lakes* with metallic bases. All the mordant colours are acidic in

nature, and the lakes they form with aluminium, chrome, iron, and other mordants are, in reality, insoluble colour salts of these metals.

It is not possible in a book devoted to the practical application of colouring-matters to deal even cursorily with the chemical operations involved in their manufacture. The subject, though of great interest, is outside the immediate purpose of this work and is too far reaching to be considered here. For full details of the chemical composition and constitution of dyestuffs, the standard works on the subject must be consulted.[1]

In practice it is usual to distinguish between the alizarins and the rest of the mordant colours. As regards application the distinction is useful, and will be observed in the following descriptions of processes.

Alizarin is the best type of mordant colour, inasmuch as it yields the brightest, fastest, and most varied range of colours with different mordants. Its alumina lake is red; its iron lake black or purple, according to the strength of the iron; its tin lake is orange; its chromium lake a rich claret shade; and its mixed alumina and iron lake a strong, deep, full chocolate, which can be made to approach black or red by increasing or diminishing the proportion of the iron to the alumina. A fine chocolate is also obtained from a mixed chromium and iron mordant; this is usually the chocolate employed in steam work, for which it is frequently toned by the addition of a little yellow—Quercitron bark. The orange from Alizarin and tin is only utilised in the brightening of the red, to which it imports a brilliant scarlet tone; a better and purer orange is obtained from Nitro-alizarin in combination with alumina and tin. A rich, warm brown is given by Nitro-alizarin and chromium mordants, but the iron lake is of no great interest.

ALIZARIN [$C_{14}H_6O_2(OH)_2$] is the essential colouring principle of the madder root, and is prepared artificially and in large quantities from anthracene—a coal-tar product. It is a yellow powder sent out by the makers, ground up in water, in the form of a 20 per cent. paste; it is insoluble in cold water, but is so finely divided that it combines readily with its mordants on steaming, and so does not require to be dissolved in any medium before use.

Three other dyestuffs closely resembling Alizarin in their chemical composition and general properties are—(1) Anthrapurpurin, (2) Flavopurpurin, and (3) Purpurin. They all give shades of red with alumina, and behave in the same way as Alizarin towards other mordants. Alizarin itself yields a crimson shade of red; Anthrapurpurin a bright full red; Flavopurpurin a yellow and rather flat red; and Purpurin, a dull bluish red, inclining to a brownish or claret tone. Mixtures of Alizarin with Anthrapurpurin or Flavopurpurin are sold as "*blue and yellow shades of Alizarin*" respectively; and it is such mixtures that form the different commercial brands of Alizarin. Those containing a large proportion of Flavopurpurin are mostly employed for reds and brownish chocolates, while those containing more Anthrapurpurin are the best for pinks and claret shades. Pure Alizarin in combination with alumina yields deep, pure crimson shades, and with chromium, full, rich maroons; it is also the best for purples.

NITRO-ALIZARIN OR ALIZARIN ORANGE [$C_{14}H_5O_2.NO_2.(OH)_2$] is applied in the same way as Alizarin, from which it is prepared by the action of nitric acid. With alumina or stannic mordants it yields orange shades remarkable for their brilliancy, and with chromium mordants a fine orange brown. Both colours are fast to light and soap.

Most of the other mordant colours, with the exception of the vegetable dyestuffs, yield only slightly different shades of one colour, whatever the mor-

[1] *The Synthetic Dyestuffs*, Cain and Thorpe (Griffin). Wahl and Atack: *Organic Dyestuffs* (Bell).

dant used may be. Logwood is only employed with chromium and iron salts for blacks, and Persian berries and Quercitron bark give various tones of yellow with alumina and tin mordants, and in strong colours, browns with chromium mordants. In practice, no other mordants are used for the vegetable colours. Sapanwood finds a limited use in some steam chocolates, as a cheap (but loose) substitute for Alizarin.

As a general rule, the Alizarin colours yield the finest results when printed on oil-prepared cloth. The percentage of fatty matter put into the cloth will vary with the depth of the colours to be printed; and the question as to whether or not tin oleates should be introduced will also be decided by the shades to be produced. Tin compounds should be avoided whenever a bright Alizarin-iron purple is desired, as the shade would be dulled considerably by the addition of orange, due to the combination of part of the Alizarin with the tin in the prepare. A pure castor oil oleine is a good standard prepare, and can be used for all styles. For reds and pinks and most basic Aniline colours the addition of tin improves the shades, but it is not absolutely essential to the attainment of good results, and can be used or not as desired. For dark steam colours about 5 per cent. of fatty matter is applied to the cloth; for light colours, half that quantity is sufficient. The percentage refers to the strength of the solution of oleine thus:—

5 per cent. Oil Prepare.

1 part ricinoleate (or sulphoricinoleate) of soda, 25 per cent.
4 parts water.

As the cloth often absorbs its own weight of liquor, it will approximately take up the amount of fatty matter represented by the percentage of the prepare, all the water being driven off on drying.

With the exception of Alizarin reds, pinks, scarlets, and oranges, the composition of most steam printing colours is extremely simple, requiring little beyond a suitable thickening, a little acetic acid, and a single mordant. But reds, pinks, etc., are somewhat more complicated, since bright shades with Alizarin can only be obtained by a combination of alumina, tin, lime, and oil, together with tartaric, citric, or oxalic acids, either free or as salts of the mordanting bases. As a matter of fact, lime is apparently necessary to the full development of all shades obtained from Alizarin, and consequently it enters into all that are employed as self colours; it may be left out of colours used solely for the making of compound shades, though its inclusion is by no means detrimental in most cases where Alizarin blue is absent. On the whole, however, lime salts are better avoided when their presence is unnecessary, since they precipitate a large number of colouring matters, and it is not always possible to foresee what colouring matters will have to be added to a compound shade to bring it up to the required standard.

In passing, it may be noted that the mordant colours when applied by direct printing are as often called "extract colours," from the fact that originally the first steam colours were prepared from extracts of Madder, Logwood, Quercitron bark, and other vegetable colouring matters.

In the following examples of printing colours, care has been taken to select only such typical examples as have, under proper conditions, yielded consistently good results on the large scale. Beyond giving these necessary types, it would be useless to enlarge the text with a mass of practical receipts, consisting of mere modifications of those given, for although the principles involved always remain the same, their working details differ according to the varying conditions under which they are applied; and success depends upon so many factors, that each firm in adopting a process has generally to modify

it to some extent in order to ensure the best results being obtained from its existing plant, system, and methods of work.

No two firms make up their colours in exactly the same way; and consequently the recipes given below must not be taken as representing the only proportions, or even ingredients, possible to use, but must rather be regarded as a selection from the immense number of printing colours employed in actual practice.

(1) **Alizarin Red.**—This is prepared in two distinct ways: (*a*) by adding the Alizarin to a thickening containing all the essential mordants; and (*b*) by adding the mordants to a paste containing the Alizarin. In both cases the final additions must only be made immediately before printing, as a reaction takes place between the colouring matter and mordants if they are allowed to stand in contact for any lengthened period.

ALIZARIN RED A. (Alumina).

27 kilos. water.
9·5 ,, starch.
9·5 ,, 6 per cent. tragacanth thickening.

Boil, cool, and add—

9·5 kilos. chlor. oil. (See Oil Mordants.)
10·5 ,, acetate of lime 23° Tw.
8·5 ,, acetate of alumina 22° Tw.
11·5 ,, sulphocyanide of aluminium 27° Tw.
14 ,, tartrate (or oxalate) of tin.

100

When required for printing, four parts of the above paste are mixed with one part of Alizarin and (for ordinary reds) two parts of paste for reds (see Pastes):—

4 kilos. mordant paste.
2 ,, red paste or reduction.
1 ,, Alizarin 20 per cent. (yellow shade).

For very dark reds the reducing paste may be omitted. Print on oiled cloth; steam 1¼ hour, with or without pressure; wash, soap, wash.

As the result of many experiments, it has been found that by boiling the Alizarin with the thickening and adding the oil mordants hot a brighter red can be obtained with a smaller quantity of oil and tin compounds than when the latter and the Alizarin are added cold. Thus—

ALIZARIN RED B. (boiled).

47 kilos. water.
13 ,, starch.
13 ,, Alizarin 20 per cent. (yellow shade).
3 ,, acetic acid 9° Tw.

Boil, turn off steam, and at once add—

2·5 kilos. chlor. oil (see Mordants).
2·5 ,, stannic hydrate 20 per cent. paste.
2·5 ,, oxalate of tin.

Cool, and immediately before use add *cold*—

3·5 kilos. acetate of lime 23° Tw.
4 ,, nitrate of alumina 23° Tw.
10 ,, sulphocyanide of alumina 20° Tw.

100 kilos. (after boiling the thickening).

Print as above on oiled cloth, etc.

A steam Alizarin red, suitable for printing on *unoiled* cloth, has been described by P. Wilhelm (*Bull. Soc. Ind. Mulhouse*, p. 69, 1908).[1] For this purpose he adds the required amount of fatty matter to the printing colour in addition to the usual oil mordants, and overcomes its liability to precipitate the metallic mordants by employing a modified form of sulphoricinoleïc acid, together with a suitable amount of formic or lactic acids, or a mixture of the two, and a small quantity of acetate of soda.

The lactic acid is only adapted for strong reds, since it retards the development of the colour on steaming. On the other hand, formic acid can be used safely for both reds and pinks; it offers no obstacle to the formation of the colour lake on steaming, and it effectually prevents the precipitation of insoluble aluminium and calcium sulphoricinoleates.

The special sulphoricinoleïc acid mixture is prepared as follows:—

EMULSION.

450 grms. freshly made sulphoricinoleïc acid,
450 ,, 16 per cent. gum-tragacanth thickening,
100 ,, acetic acid 9° Tw.,

are beaten together and allowed to stand for six days at the ordinary temperature; then add—

8650 grms. tragacanth thickening 5 per cent.
350 ,, formic acid 92 per cent.

The whole then forms 10 kilos. of an extremely stable white emulsion, in which the fatty acid exists in a very fine state of division. Being practically insoluble and mixed with organic acids, it has no action on the other mordants until the printed goods are steamed. During the steaming it combines gradually with the mordants in presence of the cloth, and the metallic sulpholeates thus formed are fixed thoroughly on the fibre, and then behave as ordinarily towards the colouring matter (Alizarin).

The advantages claimed for the following red are—(1) that it renders unnecessary the preliminary preparation of the cloth; (2) that it is easy to work and very stable; (3) that a good Aniline black can be obtained in combination with it, since the cloth is free from all traces of alkali; (4) that the whites are less yellowish than when the cloth has been prepared in oleine; and (5) that it is as bright and fast to soaping and light as is the ordinary steam Alizarin red. For the preparation of the fastest red on unoiled cloth Wilhelm gives the following instructions, and insists upon the necessity of adding the ingredients in the order indicated:—

ALIZARIN RED (on unoiled cloth).

160 grms. starch.
150 ,, water.
100 ,, tragacanth thickening.
50 ,, acetic acid 9° Tw.
150 ,, Alizarin 20 per cent. (yellow shade).
25 ,, oleine.
25 ,, stannic sulpholeate.

Boil, cool, and add—

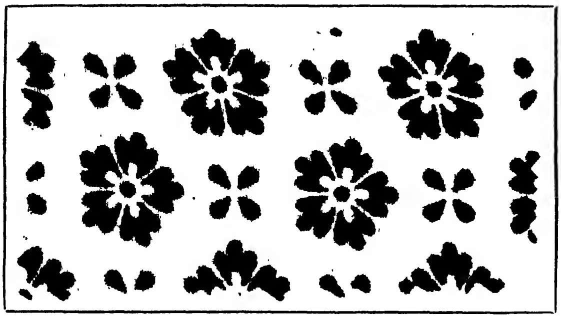
130 grms. nitrate of alumina 23° Tw.
40 ,, stannic oxalate.
75 ,, acetate of lime 23° Tw.
22 ,, formic acid 92 per cent.
100 ,, emulsion.
18 ,, acetate of soda.

Print on unprepared cloth; steam 1½ hour, and wash and soap as usual.

[1] *Journal of Soc. of Dyers and Colourists*, 1908, p. 199.

Alizarin pinks may be made in the same way, employing a blue shade of Alizarin, and reducing the standard colour to any desired extent by the addition of starch paste.

In another method, employed largely for the production of Alizarin reds on *unoiled* cloth, use is made of Lizarol D., a formaldehyde compound of ricinoleïc acid. Lizarol is insoluble in water, does not form any lake in the printing colour, and comes into action with the mordants and Alizarin in the steaming process only, forming during this process the bright red colour lake.



Alizarin Red and Pink (with Lizarol).

According to Fehling, both the mono- and polyricinoleïc acids are suitable for adding to steam Alizarin reds.[1]

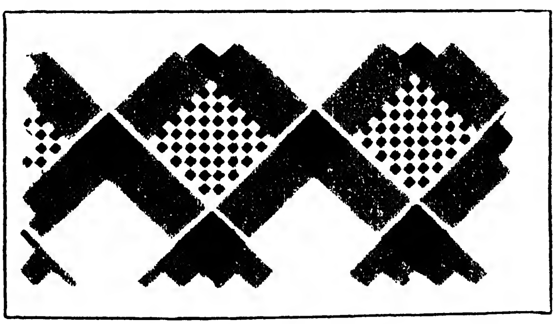
Battegay has also worked on the same subject, and has obtained the best results by adding an acetic acid solution of ricinoleïc acid to the printing paste.

Alizarin Pink may be made exactly as any of the above reds by simply employing a suitable brand of blue shade Alizarin instead of the yellow shade. Used at full strength, such pinks yield dark rich reds inclining to crimson; it is only when they are reduced considerably that true *rose pinks* are obtained. As a rule, however, Alizarin pinks differ slightly from the reds both in composition and in the proportions of their ingredients.

An Alizarin pink extensively used on the large scale in an important works is compounded as follows:—

Alizarin Pink I.

630 grms.	starch paste for reds (see Thickenings).
100 ,,	Alizarin (blue shade).
140 ,,	aluminium sulphocyanide 23° Tw.
40 ,,	acetate of lime 23° Tw.
30 ,,	oxalate of tin (stannic).
60 ,,	citrate of alumina 40° Tw.
1000	



Alizarin Red and Pink (on Oiled Cloth).

Print on oiled cloth, steam, wash, and soap. If the pink is printed as a shirting or other single colour, it is usually soaped strongly in the rope form; in other cases it passes through the open soaper at full width, as is usual with most steam work.

[1] *Rev. Gen. des Mat. Col.*, p. 74, 1909.

CITRATE OF ALUMINA 40° Tw.

500	grms.	hydrate of alumina, 15½ per cent. paste.
220	,,	citric acid.
28	,,	soda-ash.
200	,,	water.

Stir till dissolved.

A much brighter pink is obtained by adding a small quantity of the basic colour Rhodamine to the above. Rhodamine 6 G. concentrated is a pure product, and, unlike many other Rhodamines, it is not precipitated by the alumina in the printing paste, and thus it gives an even shade, free from specks. The proportions taken are—

1000	grms.	Alizarin pink I. (above).
3	,,	Rhodamine 6 G. concentrated.
50	,,	acetic acid 6° Tw.

Blotch pinks, or pinks used for the printing of grounds, and stipple engraving, are made up with either starch, starch and gum tragacanth, British gum, or Senegal gum. The last always gives the best results, and is invariably used when its price is no obstacle. Starch is apt to give a "mealy" surface, and even when mixed with tragacanth it almost always requires to be "crushed," *i.e.* the printed cloth must be passed under a plain unengraved roller working in starch paste—a crush roller—in order to obtain a perfectly smooth, even blotch. Tragacanth alone is an excellent thickening to use for many qualities of cloth, but gum Senegal produces the finest results in all cases, and is a reliable thickening on all kinds of cloth.

As a rule, the quantity of mordant to a given weight of Alizarin is proportionally greater in pinks than in reds, the reason being that as they are reduced or diluted they require extra mordant to bring about their full development in steaming. The extra mordant may be added to either the standard colour or to the reducing paste; the former is the more usual and more convenient method.

GUM ALIZARIN PINK II. (for blotches).

630	grms.	gum Senegal solution 50 per cent.
100	,,	Alizarin (blue shade) 20 per cent.

Mix well and add—

30	grms.	stannic oxalate.
40	,,	acetate of lime 23° Tw.
60	,,	citrate of alumina 40° Tw.
140	,,	sulphocyanide of aluminium 23° Tw.
1000		

Print on oiled cloth; steam, etc., as usual.

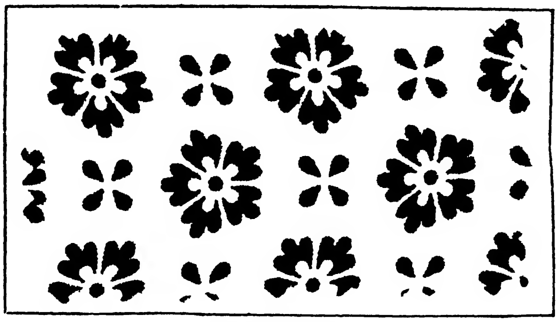
For light shades the above pink is merely reduced by the addition of gum Senegal. Thus—

	Medium Pink.	*Pale Pink.*
Standard Pink	1	1
Gum Senegal 30 per cent. .	9	40 or more.

Acetate, nitrate-acetate, or nitrate of alumina may be used instead of the sulphocyanide, but, for the most part, the latter is preferred because it does

not attack the doctors, and thus prevents the dulling of the shade from dissolved iron. The nitrate and nitrate-acetates tend to impart a yellowish tone to the pink, and are sometimes employed expressly for that purpose. A similar effect may be obtained by using a yellower brand of Alizarin, but in general the shade of pink is not so bright as when nitrate of alumina is employed, since, apart from the shading and brightening properties of the latter, the yellow brands of Alizarin yield colours somewhat dull in character.

"Cover" reds and pinks, and their resists, will form part of a separate division.



Alizarin Claret.

Alizarin Claret (Chrome).—The Alizarin chrome lake is employed largely as a blotch in cretonne printing, and as a constituent of an enormous number of extract browns, greys, olives, etc. For blotch work it may be made as follows, the lake, of course, being produced by steaming:—

Steam Alizarin Claret A.

140	grms.	starch.
300	,,	water.
50	,,	acetic acid 9° Tw.
240	,,	gum-tragacanth thickening 5 per cent.
180	,,	Alizarin I.P.p. 20 per cent. (British Alizarin Co., Ltd.).
30	,,	cotton-seed oil.
Boil, cool, and add—		
70	grms.	acetate of lime 23° Tw.
90	,,	acetate of chrome 25° Tw.
1100 = 1000 after boiling.		

Print on oiled cloth, and steam, etc., as for reds. Steam Alizarin claret enters largely into a great many compound tertiary shades; and as many of the colours associated with it in this connection are precipitated by acetate of lime, this latter must be omitted in all clarets used for mixtures.

Steam Alizarin Claret B. (for mixtures).

745	grms.	acid starch paste.
150	,,	Alizarin I.P.p. 20 per cent. (British Alizarin Co., Ltd.).
75	,,	acetate of chrome 24° Tw.
30	,,	cotton-seed oil.
1000		

The shades of claret may be varied by using different brands of Alizarin, or by adding other mordant colours, or by mixing aluminium and chromium mordants together.

The Alizarin Bordeaux also yield fine shades of claret, and, as they are fixed with alumina, they may be used to modify the shade of steam Alizarin reds, without unduly dulling the colour.

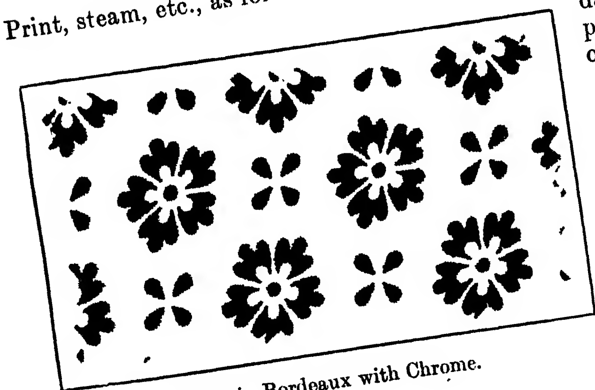
Alizarin Bordeaux with Alumina.

STEAM ALIZARIN BORDEAUX (red shade).

105 grms.	Alizarin Bordeaux paste.
100 ,,	water.
645 ,,	starch-tragacanth thickening.
70 ,,	sulphocyanide of aluminium 18° Tw.
50 ,,	acetate of lime 23° Tw.
20 ,,	castor oil.
10 ,,	oxalate of tin 25° Tw.
1000	

Print, steam, etc., as for reds.

With chromium mordants Alizarin Bordeaux paste yields quiet shades of lilac.



Alizarin Bordeaux with Chrome.

Steam Alizarin Purple (Iron).—Steam Alizarin purples or violets have lost much of their importance since the introduction of Modern violets and other chrome violets too numerous to mention. They are, however, still largely used for some purposes for which their fastness renders them difficult of replacement. Steam Alizarin purples are frequently brightened by the addition of Methyl violet.

ALIZARIN PURPLE A.

565 grms.	acid starch paste.
170 ,,	Alizarin (blue shade) 20 per cent.
110 ,,	acetate of lime 23 per cent.
85 ,,	pyrolignite of iron 32° Tw.
10 ,,	Methyl violet B. extra.
60 ,,	acetic acid $1\frac{1}{2}$° Tw.
1000	

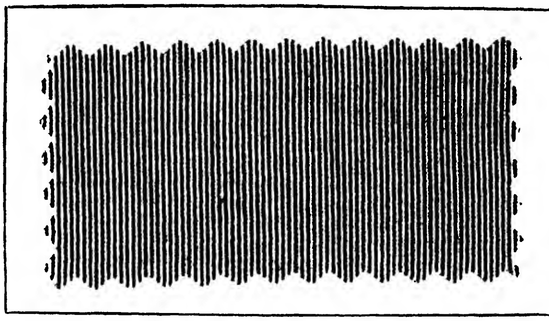
Print on oiled cloth, steam, wash, and soap.

For light purples or lavenders, pyrolignite of iron is often replaced by potassium ferrocyanide.

LIGHT STEAM ALIZARIN PURPLE B.

696 grms. acid starch paste.
15 grms. Alizarin (blue shade) 20 per cent.
200 grms. gum tragacanth 5 per cent.
15 grms. acetate of lime 23° Tw.
4 grms. potassium ferrocyanide, in—
70 grms. water.

——
1000



Steam Alizarin Purple.

Print, etc., as for reds.

A brighter shade results from the addition of 0·75 grm. of Methyl violet to the above.

Steam Alizarin Chocolate.—Used alone with any single mordant, Alizarin does not give a good shade of chocolate, but when toned with a little Quercitron bark extract, and fixed with chrome and iron, it produces a very fine, fast shade, useful alike for blotches, fine outlines, objects of any size, and mixtures.

CHOCOLATE A.

300 grms. water.
175 ,, tragacanth thickening 4 per cent.
75 ,, starch.
50 ,, acetic acid.
40 ,, cotton-seed oil.
160 ,, Alizarin I.P.p. 20 per cent.
60 ,, Quercitron bark extract 48° Tw.

Boil, turn off steam, and add—

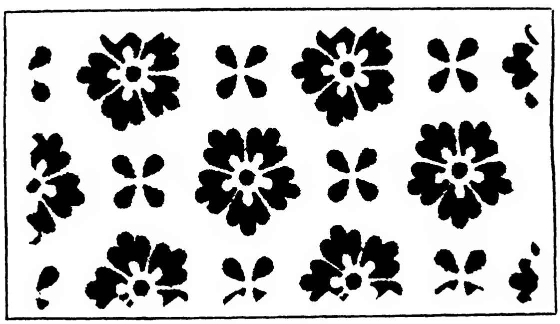
15 grms. yellow prussiate of potash (ground).

Allow time to dissolve; then cool and add—

75 grms. acetate of lime 23° Tw.
150 ,, acetate of chrome 18° Tw.

——
1100 = 1000 after boiling.

Print on oiled cloth, steam, wash, and soap.



Alizarin Chocolate.

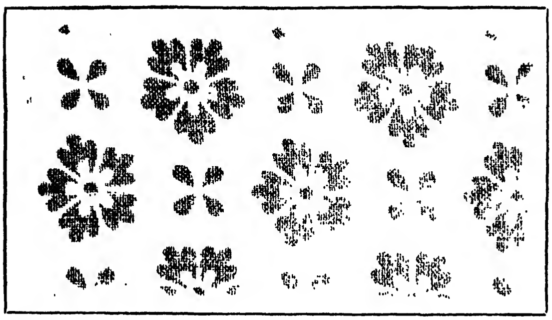
The foregoing chocolate is for blotches and large objects for which a soft, thinnish colour is required. For finer engraving and general work it may be thickened with starch, with or without the addition of a little British gum. The gum helps to improve its working qualities, which, in common with all strong Alizarin colours, are not too good when it is used at full strength.

In conjunction with Persian berry or Quercitron bark extracts, the above

chocolate gives a fine range of useful browns, and affords a convenient means of darkening many colours without the actual addition of black, which always has the effect of deadening even dark shades.

(2) **Other Alizarin Colours.**—Among these are the Nitro-alizarins or Alizarin oranges, Alizarin maroon, Alizarin blue, and a great number of other anthraquinone and analogous derivatives, known under the general names of Alizarin yellows, blues, greens, browns, and blacks, and all fixed in a similar way.

ORANGE (NITRO-ALIZARIN).—This colour is a beautiful pure orange, and forms the point of departure for a large variety of salmons, terra-cottas, and other mixed shades. For printing as an orange it is made as under:—



Alizarin Orange (Alumina).

ALIZARIN ORANGE (bright).

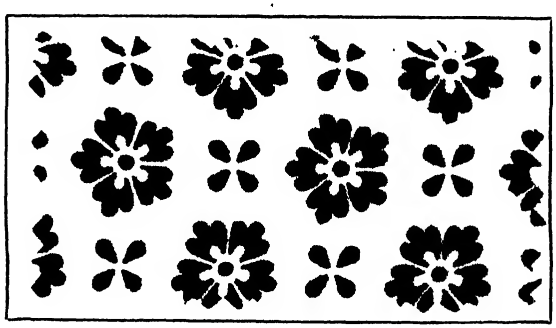
420	grms.	acid starch paste.
200	,,	gum tragacanth 2 per cent.
100	,,	Alizarin orange 20 per cent.
200	,,	nitrate of alumina 20° Tw.
50	,,	acetate of lime 23° Tw.
30	,,	oxalate of tin.
1000		

For salmon shades the above orange is mixed in various proportions with steam Alizarin pink.

A browner shade of orange is obtained by reducing a colour made up with a chromium mordant—a colour which in strong shades is a warm chestnut brown.

ALIZARIN ORANGE (with Chrome).

700	grms.	acid starch paste.
150	,,	Alizarin orange 20 per cent.
75	,,	acetate of chrome 25° Tw.
45	,,	acetate of lime 23° Tw.
30	,,	olive or cotton-seed oil.
1000		



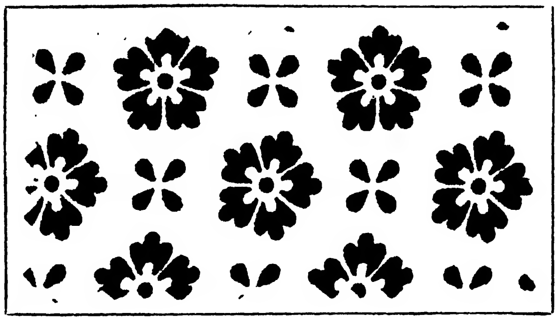
Alizarin Orange (Chrome).

For mixtures with Alizarin blues and yellows, the acetate of lime is left out of the above.

The Alizarin oranges are printed on oiled cloth, and treated exactly as the reds.

ALIZARIN BLUE.—Alizarin blue comes into the market in different forms, some of which are soluble and others insoluble in water. The bisulphite com-

pounds—Alizarin blue S., and S.B., and S.R.X., in powder, and S. 2 R. in paste — are those most usually employed. They are extremely soluble in cold water, and can be added directly to the thickening paste without previous solution. The Anthracene blues are similar in properties to the Alizarin blues, and are applied in precisely the same way. The following recipes for Alizarin blue S. will serve for all others belonging to the same class.



Alizarin Blue S. (I.C.I.).

Alizarin Blue I. (Chrome).

50 grms. Alizarin blue S. Powder.
650 ,, starch paste.
150 ,, 4 per cent. gum tragacanth.
150 ,, acetate of chrome 25° Tw.
———
1000

Alizarin Blue II. (Zinc).

60 grms. Alizarin blue S.
820 ,, starch paste.
120 ,, zinc sulphate ($ZnSO_4.7H_2O$).
———
1000

Dissolve in the cold.

Alizarin Blue III. (with Nickel).

60 grms. Alizarin blue S.
820 ,, starch paste.
120 ,, acetate of nickel 15° Tw.
———
1000

Alizarin Blue IV. (with Copper).

60 grms. Alizarin blue S.
820 ,, starch paste.
120 ,, acetate of copper 15° Tw.
———
1000

Print on oiled cloth, steam, wash, and soap.

The chromium and copper lakes of Alizarin blue are by far the fastest in every respect; in light shades the copper lake is the faster of the two, especially to light. The zinc and nickel lakes are greener and much more pleasing in tone than the preceding, but they lack resistance to the action of light, fading to bluish and reddish greys after an exposure of twelve days to moderate sunlight. Along with mordant yellows and Alizarin claret, Alizarin blue is largely used for the production of all shades of olive, brown, grey, and other mode or tertiary shade.

CHROME COLOURS.

With the exception of a few Alizarin colours, the vegetable colours and the nitroso compounds (Resorcin green, etc.), all the mordant colours are fixed, practically exclusively, with chromium mordants—hence the designation *Chrome colours.* Chrome mordants give the fastest and, generally, the most beautiful lakes obtainable from these colours, though occasionally iron, alumina, and tin mordants are made use of for the production of duller (and usually looser) effects. With Modern yellow and analogous dyestuffs, tin and alumina mordants in combination give exceedingly *brilliant* yellows, which, however, leave a great deal to be desired in the way of fastness to light and soaping. On the other hand, every mordant in general use, with the sole exceptions of alumina and tin, yields bright and fast colours with the nitroso group of dyestuffs. These colours also differ from the usual chrome colours in forming differently coloured lakes with the respective mordants. For instance, dinitroso resorcin gives a dark green with iron; a brown with chrome; a yellow with nickel; and an orange-brown with cobalt—all very fast to light and soaping.

The great majority of the chrome colours give only variations of the same colour whatever mordant be used with them; and as chromium mordants give the finest and fastest shades they are the most extensively employed, chromium-acetate being the general group mordant. The formiates, lactates, and glycollates of chromium are suitable for some classes of work, and in certain instances the sulphocyanide and bisulphite are to be preferred. Occasionally, too, the addition of an oil mordant, such as oleine or lizarol, is beneficial in the way of enhancing the brightness of the shade and improving the working qualities of the colour, though, generally speaking, better results are obtainable in the absence of oil.

On oil-prepared cloth the colours are usually much looser and frequently also duller than on plain bleached cloth, so that, unless they have to work in association with Alizarin reds and pinks, it is safer and cheaper to avoid oil mordants in any form. A few colours, however, are *improved* by the presence of oil mordants; and in any case the effect of oil preparations is not so detrimental as to preclude the use of any chrome colour in any steam style.

On naphthol prepared goods many of the chrome colours, especially those of the Modern and Ultra series (oxazines, gallocyanine, or pyrogallol derivatives), are fixed easily by a short steaming owing to the almost instantaneous neutralisation of the acid of the mordant by the alkali and oil in the prepare whereby the metallic base is liberated and combines at once with the colouring matter.

The preparation of the printing colours is very simple, involving no tedious preliminary operations, save in a few instances where certain colouring matters are used in their original insoluble forms, such, for example, as Alizarin and Gallamine blues and Cœrulein. These colours merely require a few hours steeping in sodium bisulphite to render them soluble, and even this is not necessary if the brands marked S.—the bisulphite compounds—are taken in the first instance.

The majority of the chrome colours are applied in the same way as Alizarin blue S. The percentage of colouring matter may vary according to its concentration, and the depth of shade required, and the proportion of mordant will have to be adjusted so as to supply the requisite amount of metallic oxide to fix completely the whole of the colouring matter, but in other respects nearly all the colours may be made-up on the lines of Alizarin blue S.

The printing paste consists essentially of colouring matter, thickening,

acetic or other organic acid, and acetate of chrome. Slight additions of other ingredients are made in particular instances, and will be noted as they occur; in some cases, too, acetic acid is omitted. In making up a printing colour the usual procedure is to dissolve, first of all, the colouring matter in the acetic acid and water; then add the warm thickening gradually, stirring all the time until the mixture is perfectly smooth and homogeneous; finally cool and add the necessary mordant. After straining, the colour is ready for printing.

The formulæ given hereafter are typical of the methods employed in the application of the different series of chrome colours, and the colours mentioned are good representatives of their respective classes.

The **Azo series** consists of combinations of various diazotised or tetrazotised amido bases, with salicylic acid and its derivatives, and is represented by Alizarin (so-called) and Diamond yellows, Diamond flavine, etc., all of which may be made up as under:—

ALIZARIN YELLOW R.

200	grms.	Alizarin yellow R. 20 per cent. paste.
655	,,	starch-tragacanth thickening.
125	,,	acetate of chrome 32° Tw.
20	,,	cotton-seed oil.
1000		

Alizarin yellows R. and G.G. are made by coupling the diazo salts of *p*-nitraniline and *m*-nitraniline respectively with salicylic acid. Diamond yellows R. and G. are prepared in like manner from salicylic acid and the diazo salts of *o*- and *m*-aminobenzoic acids respectively. These colours, though closely related to the Acid-azo dyestuffs, both chemically and by their mode of formation, are nevertheless true Chrome colours owing to the fact that the OH and COOH groups in the salicylic acid residues occupy the *ortho*-position to each other—a position which endows the colours with mordant properties.

Calico yellow, Salicine yellows, Diamond flavine, etc., are all prepared similarly. These colours range in shade from a greenish sulphur to a deep orange; and to a great extent they have displaced the vegetable yellows especially in the making of compound shades like olives and mode colours.

Anthracene, Modern and Xantharine yellows, though not identical with the above, are applied in the same way. They form lakes with chromium, tin, and aluminium mordants. The chromium lakes are the fastest in every respect; those resulting from mixtures of tin and aluminium give exceedingly brilliant yellows suitable for a variety of purposes, but of inferior fastness.

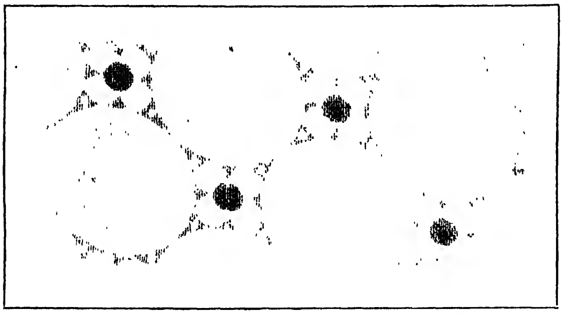
ANTHRACENE YELLOW.

{ 40	grms.	Anthracene yellow (Geigy).
{ 40	,,	acetic acid.
{ 80	,,	water.
700	,,	starch-tragacanth paste.
100	,,	acetate of alumina 22° Tw.
40	,,	stannous hydrate 50 per cent. paste.
1000		

Print on oiled cloth, steam one hour, wash and soap if necessary.

The Chromocitronines of various shades (D. & H.), Calico flavine (Geigy), and the corresponding Gallo yellow, are all derivatives of salicylic acid, and they differ from the commoner Alizarin yellows in being of quite exceptional fastness. In their remarkable resistance to the action of light, soap, alkalies, acids, and bleaching powder they are unsurpassed; in fact they are amongst the most permanent of all mordant colours.

Chromocitronine V., the greenest yellow of the series, is very pure in tone, and is particularly suited for the production of pure bright greens when mixed with Alizarin green S. or Chromazurine D.N.



Chromocitronines 3 R. and V.

CHROMOCITRONINE (R., 3 R., V.).

25 grms. Chromocitronine.
180 grms. water.
670 grms. starch-tragacanth paste.
50 grms. acetic acid 40 per cent.
75 grms. acetate of chrome 32° Tw.

1000

Print, steam, wash, and soap.

The **Oxazine series** comprises a great number of valuable dyestuffs, fixed by chrome mordants, of which Gallocyanine is the type. Gallocyanine itself is prepared by condensing nitrosodimethylaniline with gallic acid; other members of the series are obtained by varying the nitroso and phenolic components, and also by further treatment of gallocyanines.

Modern violet, Modern blue, Blue 1900, Ultra violet, and analogous products, derivatives of Gallocyanine, which form leuco compounds, or are put on the market as such, are excellent colours for blotch work. They possess both acid and basic properties, and, consequently, they may be shaded or toned with any of the basic colours, since they are fixed almost as well by tannic acid as by chromium mordants. Usually both mordants are used in combination, especially in the case of Modern violet. The addition of hydrosulphite-formaldehyde, in small quantity, is also beneficial, as it prevents the premature oxidation of the leuco compound, and thus promotes evenness of shade. Tannic acid has the effect of *bluing* the shade of the chromium lake, which is too red in tone for navy blotches. As an example of this class of colour the following will serve:—

DARK NAVY BLUE (blotch).

3,500 grms. Modern violet powder (D. & H.)
1,500 ,, Setoglaucine (basic colour) (Geigy).
8,000 ,, acetic acid 9° Tw.
2,000 ,, acetine.
10,000 ,, water.
31,700 ,, water.
10,000 ,, starch.
4,500 ,, tragacanth thickening 5 per cent.
300 ,, cotton-seed oil.
3,500 ,, hydrosulphite-formaldehyde 50 per cent. solution.

Boil, cool, and add—

3,000 grms. Alizarin oil 25 per cent.
10,000 ,, tannic acid 1 : 1 (=50 per cent.).
12,000 ,, acetate of chrome 15° Tw.

100,000 grms. after boiling.

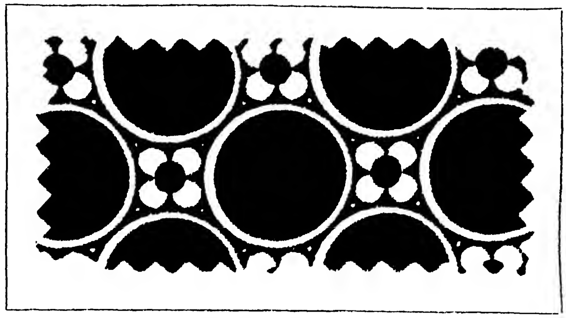
Print, steam, allow to lie a short time, and then wash and soap as usual.

Modern violet alone is printed as under:—

MODERN VIOLET.

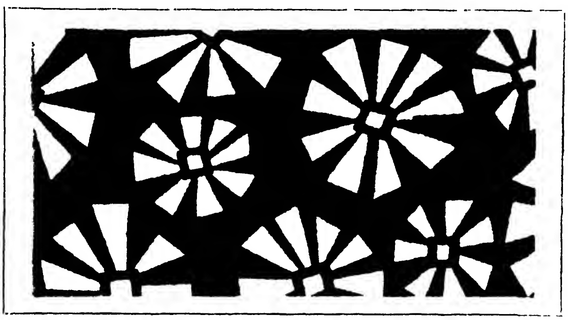
30 grms. Modern violet O. powder (D. & H.).
200 grms. boiling water.
645 grms. starch-tragacanth paste.
25 grms. acetic acid 60 per cent.
100 grms. acetate of chrome 23° Tw.

1000



Modern Violet O.

A little hydrosulphite may be added if desired; it tends to equalise the shade. Print, steam, wash, etc., as above.



Chrome Violet.

Other similar violets are: Modern heliotrope (D. & H.); Ultra violet M.O. (Sandoz); Anthraquinone violet (L.B.H.); Chrome violet pdr. (Geigy); and others, not all of which are of quite the same group. Chrome violet, a very red shade, for example, is a condensation product of formaldehyde and salicylic acid.

CHROME VIOLET.

30	grms.	Chrome violet (Geigy).
160	,,	water.
60	,,	acetic acid 6° Tw.
600	,,	starch-tragacanth paste.
30	,,	acetine.
120	,,	acetate of chrome 18° Tw.
1000		

Print, steam, and wash.

Other violets may be printed in the same way or like Modern violet.

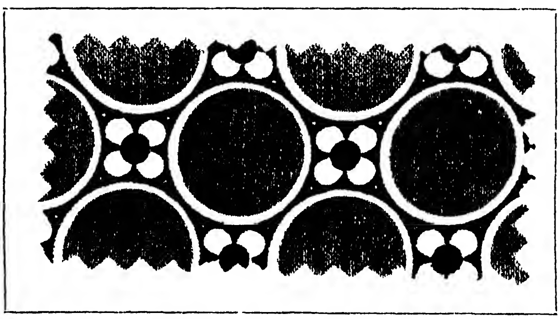
The **Chrome blues** are a very important and numerous group of mordant colours. The greater number of the best and fastest of them belong to the oxazine series, and such as do not, may, for the sake of convenience, be classed with them as they are applied by similar methods.

The best-known members of the group are perhaps Modern blue C.V.I., Chromacetine S., Brilliant fast cyanine R., the Chromophenines, Phenocyanines, and Chromazurines (D. & H.); the Ultracyanines, Ultra-alizarin S., Brilliant Delphine blue B., and Gallo blue B. (Sandoz); Anthracene blue and Fast chrome blues G. & R. (I.C.I.); Gallamine blue (Geigy); and the Anthracene blues (L.B.H.). The Gallo blues are practically identical with the Modern colours; but they offer no advantage over their better-known competitors. The Chromazurines give very bright blues—Chromazurine E. is the purest of all, being almost equal in this respect to Methylene blue—and apart from their use as self shades, they enter largely into the composition of fast and bright greens and olives.

With Chromazurol S. (Geigy), another member of the mordant group, a particularly fine bright medium blue is obtained which finds a wide application in certain styles of printing, though it leaves something to be desired as regards fastness to light.

Many other excellent chrome blues are in current use; and also some, such as the Indian blues—mixtures of reduced logwood and basic colours—which are best avoided except for the cheapest classes of work on low cloth for which depth of shade is more important than fastness.

It has not been thought necessary to give a full list of the Chrome blues, as the methods of application are very similar in all cases. Any competent colour-mixer can easily modify his recipe according to requirements.



Brilliant Fast Cyanine R.

The following typical formulæ will serve to illustrate the general methods of applying Chrome blues:—

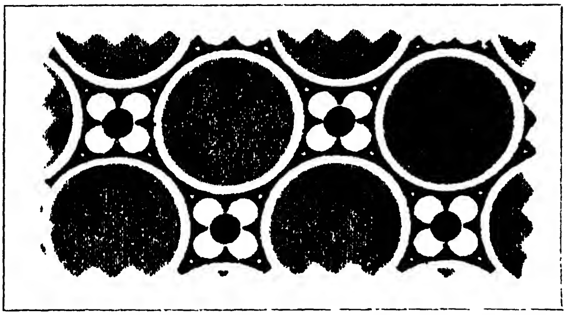
BRILLIANT FAST CYANINE R.

60	grms.	Brilliant fast cyanine R. (D. & H.).
175	,,	water.
565	,,	starch-tragacanth paste.
30	,,	formic acid 85 per cent.
170	,,	acetate of chrome 32° Tw.
1000		

Chromacetine S. may also be printed according to this recipe.

CHROMAZURINE D.N.

30 grms.	Chromazurine D.N. (D. & H.).
250 ,,	boiling water.
20 ,,	glycerine.
525 ,,	thick starch-tragacanth paste.
75 ,,	olive oil.
25 ,,	acetic acid 40 per cent.
75 ,,	acetate of chrome.
1000	



Chromazurine D.N.

The addition of oil and glycerine intensifies dark shades of Chromazurines considerably, especially those of the G. brand; its effect in light shades is scarcely perceptible.

Modern cyanine V. is the greenest of the Chrome blues.

The oxazine greens, Ultraviridine, and Alizarin greens B. and G. will be dealt with under *mordant greens*.

Oxyketone colours find little application at present. They are represented by only three colours in practice, viz. Alizarin yellows A. and C. and Alizarin black S. The latter is restricted to the production of grey shades of excellent fastness.

ALIZARIN BLACK S.

150 grms.	Alizarin black S. paste.
660 ,,	starch-tragacanth paste.
150 ,,	acetate of chrome 20° Tw.
40 ,,	cotton-seed oil.
1000	

Print and steam, etc.

The Alizarin yellows of this group are applied similarly.

The **Phthaleïn group** of mordant colours consists of two members only: Galleïn, a purple used for dyeing, and Cœruleïn, a valuable olive colouring matter, derived from Galleïn, and employed largely for printing cretonne blotches. The latter will be dealt with under *mordant greens*.

Chrome Reds.—Most of these colours are merely mixtures of Alizarin yellows with various proportions of Rhodamine 6 G. Such mixtures are easily made in any printworks, and require no special description. The Rhodamines themselves, though really basic colours, are capable of forming lakes with

both chromium and aluminium mordants, and are as often used in this way as with tannic acid. The shades are much brighter but looser.

Chromorhodines J. and B. and Chromopurpurine J.J. are true Chrome reds which *cannot* be fixed with tannic acid, though they are closely akin to the basic Rhodamines in general properties. They are, perhaps, somewhat faster to soaping than the Rhodamine chrome lakes, and they yield equally brilliant shades, but in no sense can they be regarded as *fast colours*. In common with the Rhodamines and other Chrome reds they are out of place in a group of such all-round excellence as the mordant colours.

Chrome Greens.—These colours include members of several groups such as: Alizarin viridine, Alizurol green, Alizarin green S., Alizarin cyanine green (Anthraquinone); Ultraviridine, Alizarin green B., Alizarin green G. (oxazone); Cœruleïn (phthaleïn); and Gallazol green F.D. bluish, Modern olive and various other Chrome greens. All these colours produce fast lakes with chromium oxide, and are used largely both as self colours and as constituents of a great number of compound shades.

Cœruleïn Olive I.

200 grms.	Cœruleïn S. paste (bisulphite compound).
150 ,,	water.
500 ,,	thick starch-tragacanth paste.
150 ,,	acetate of chrome 32° Tw.
1000	

Cœruleïn Olive II.

50 grms.	Cœruleïn conc. powder.
150 ,,	water.
100 ,,	bisulphite of soda 66° Tw.

Allow to act two to three days, then add—

550 grms.	thick starch-tragacanth paste.
150 ,,	acetate of chrome 32° Tw.
1000	

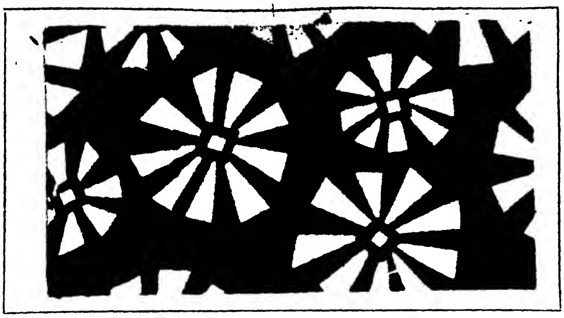
Alizarin Green S.

150 grms.	Alizarin green S. (paste).
660 ,,	starch-tragacanth paste.
150 ,,	acetate of chrome 20° Tw.
40 ,,	cotton-seed oil.
1000	

Bisulphites of chrome and nickel may also be used as mordants.

Gallazol Green F.D. Bluish Paste.

200 grms.	Gallazol green F.D.
50 ,,	water.
50 ,,	formic acid 85 per cent.
525 ,,	starch-tragacanth paste.
175 ,,	acetate of chrome 32° Tw.
1000	



Gallazol Green F.D. Bluish (Geigy).

ALIZARIN VIRIDINE.

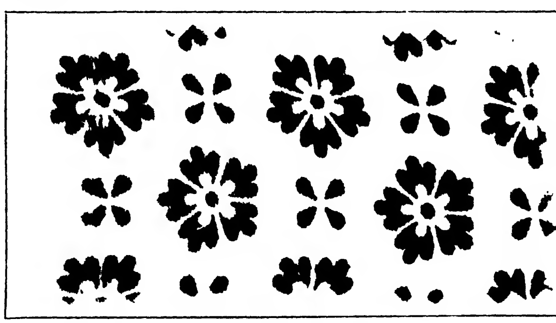
40	grms.	Alizarin viridine (or 200 grms. Alizurol green 20 per cent. paste).
150	,,	water.
70	,,	formic acid 85 per cent.
120	,,	starch.
400	,,	water.
20	,,	cotton-seed oil.

Boil, cool, and add—

200	grms.	acetate of chrome 32° Tw.
1000		

Alizurol green and Alizarin viridine are the brightest and purest greens of their class, Cœruleïn being a deep olive and Alizarin green S. inclining to a dull blue, especially in light shades. All are printed on oiled cloth, and then steamed, etc., as for Alizarin reds.

Anthracene (or Alizarin) and Chrome Browns and Greys.—ANTHRACENE BROWN gives a useful shade of dull dark brown, employed sometimes as a self colour, but more frequently to tone down compound shades.

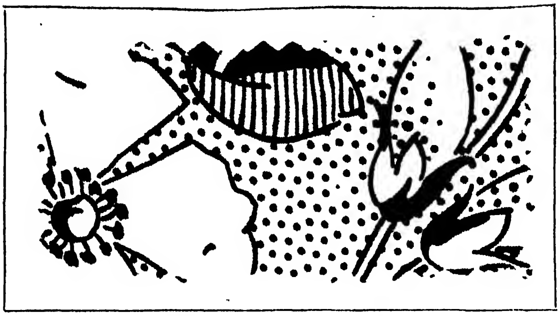


Anthracene Brown W.L.S. (I.C.I.) (Alumina).

Anthracene brown produces very fast lakes with both aluminium and chromium mordants. The aluminium compound is reddish; that with chromium is somewhat yellower and much duller, but at the same time faster to washing and much more generally useful.

ANTHRACENE (OR ALIZARIN) BROWNS.

I.	120	grms.	Alizarin brown H.D. powder (I.G.).
	50	,,	Glyecine A.
	230	,,	hot water.
	450	,,	starch-tragacanth thickening.
	50	,,	acetic acid 50 per cent.
	100	,,	acetate of chrome 32° Tw.
	1000		



Alizarin Brown H.D. (I.G.)

II. 70	grms.	Anthracene brown G. 20 per cent.
20	,,	acetic acid 9° Tw.
720	,,	starch paste.
150	,,	acetate of alumina 15° Tw.
40	,,	oxalate of tin.
1000		

Oxalate of tin helps to brighten the shade, but it may be omitted if desired.

In combination with Persian berry extract, or Quercitron bark extract, Anthracene brown yields a range of fine quiet mode shades, varying from the deepest dull brown to pale buffs.

BROWN A.P.B. (dark).

150	grms.	Anthracene brown G. 20 per cent.
15	,,	Persian berry extract 48° Tw.
560	,,	starch-tragacanth paste.
250	,,	acetate of chrome 15° Tw.
25	,,	acetate of lime 23° Tw.
1000		

Print, steam, wash, and soap.

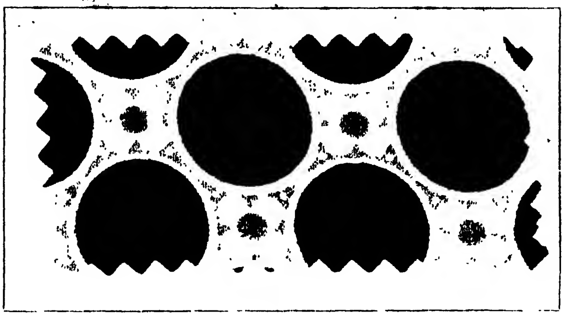
Other Alizarin colours may also be mixed with Anthracene brown in any proportion for the production of a great variety of subdued tints fast to light and soap. In fact nearly all greys, olives, fawns, and other mode shades are obtained by mixing a few standard colours in various proportions ; and one of the most important is Anthracene brown, by reason of its fastness and the facility which it affords for flattening a tint without altering its character to the extent that black or blue would do.

A point to be noted in connection with Anthracene and Alizarin browns and their mixtures with other colours, is that they require to be thoroughly well steamed in order to effect their full fixation ; 1¼ to 1½ hours is not too long. If this is not done the colours come up weak and uneven in shade.

A colour of exceptional interest to calico printers is the recently introduced **Chrome Deep Brown A.G. (D. & H.).** It is a soluble colour, works well in the printing machine, and is easily and completely fixed by the usual 45 minutes' steaming. It yields dark rich chestnut brown shades of good all-round fastness, and it possesses the excellent property of neither subliming nor marking-off during the steaming process—a defect very common in Alizarin mixtures and many other dark steam browns.

CHROME DEEP BROWN A.G.

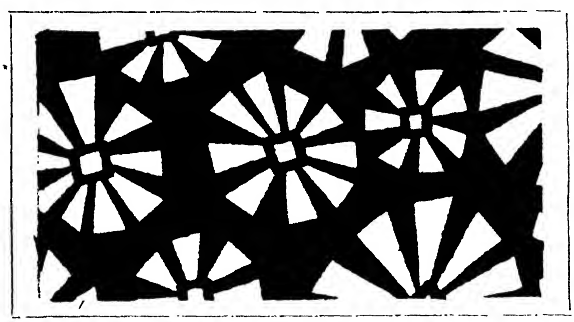
40	grms.	Chrome deep Brown A.G. (D. & H.).
150	,,	water.
25	,,	acetic acid 9° Tw.
635	,,	starch-tragacanth paste.
150	,,	acetate of chrome 32° Tw.
1000		



Chrome Deep Brown A.G. 4 per cent.
,, Fast Xanthine 2 R. 1¼ per cent.

Chrome Fast Xanthine 2 R., of which a light shade is shown printed alongside Chrome deep brown A.G., is a bright and fast orange, largely used in all classes of steam styles. It may be printed according to the foregoing recipe and reduced to 1¼ per cent. of colour.

Azochromine is a useful reddish-brown particularly adapted, in addition to ordinary direct printing, to printing on β-naphthol prepare along with Para red, etc. It is obtained by coupling diazoaminophenol with pyrogallol and is fixed by chromium mordants in steaming. A short steaming of 3–4 minutes is sufficient for its fixation.

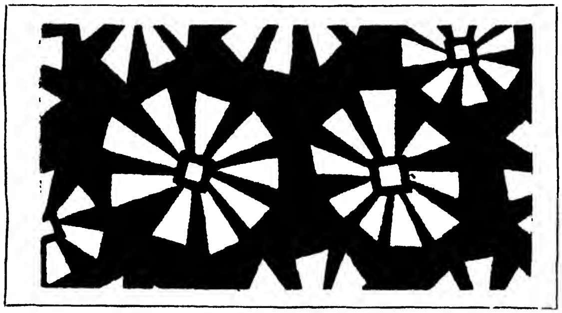


Azochromine (Geigy).

AZOCHROMINE.

150	grms.	Azochromine in paste (Geigy).
50	,,	water.
25	,,	acetic acid 9° Tw.
625	,,	starch-tragacanth paste.
150	,,	acetate of chrome 32° Tw.
1000		

Amongst the Chrome greys it is only necessary to mention Modern grey R.C.N. (D. & H.), and Chrome grey N. (Geigy). They are applied by any of the foregoing formulæ containing simply acetate of chrome and acetic acid. Modern grey R.C.N. and Chrome grey N. give the best results for most purposes, nearly all other chrome greys possessing the disadvantage of causing a yellow discoloration on the back of the print and frequently also on the face of it as well.



Chrome Grey N. 1½ per cent.

Chrome Grey N.

15	grms. Chrome grey N. (Geigy).
250	grms. water.
25	grms. acetic acid 9° Tw.
660	grms. starch-tragacanth paste.
50	grms. acetate of chrome 32° Tw.
1000	

Nitroso or Quinoneoxime Colours.—These are all nitroso compounds of either resorcin, α-naphthol, β-naphthol, or dihydroxynaphthalene. They come into the market under various names, of which the following are the best known: Resorcin green, Solid green O., Fast myrtle; Fast steam green, Ferro green, Fast green T.; Gambine Y. & G., Dioxine, Nitrosine D.H., Nitrosine N.N., and Chrome bistre.

If desired they can be easily and cheaply prepared in the works without any necessity for special plant. The manufacture of dinitrosoresorcin (Resorcin green) will serve to indicate the general procedure:—

Dinitrosoresorcin 25 per cent. paste.

500	grms.	resorcin $C_6H_4(OH)_2$.
3000	,,	water. Dissolve with heat and add—
650	,,	sodium nitrite 94 per cent. $NaNO_2$. Cool and add—
3000	,,	ice; then run in gradually
700	,,	sulphuric acid 123° Tw.

Stir continually and keep the temperature down by adding fresh ice if necessary. The nitroso product separates out as a finely divided precipitate. Wash 2–3 times by decantation and filter to 3050 grms. = 25 per cent. paste.

With iron mordants the above yields dark myrtle greens; with chrome and alkaline copper mordants, dark browns; with cobalt mordants, orange browns; and with nickel mordants, dull yellows. All these colours are fast to light and soap. The iron and chromium colours are the most generally employed, and the latter forms a useful dark-brown blotch in ordinary steam work, and a pleasing series of lighter browns and fawns when reduced in strength. It may be printed on oiled or unoiled cloth, the former giving a slightly better result. On the whole there is not a great deal of difference between the two shades, and it is practically immaterial upon which cloth the colours are printed.

Green D.R.

100 grms. dinitrosoresorcin 25 per cent. paste.
100 ,, water.
100 ,, 25 per cent. ammonia.

Dissolve and add in the cold—

25 grms. glycerine.
580 ,, starch-tragacanth paste.
95 ,, potassium ferrocyanide (ground).

1000

Stir till the ferrocyanide is dissolved, then strain and print.

Sulphocyanide or acetate of iron, or Mohr's salt, may also be used as mordants.

Fast Green T.

80 grms. Fast green T. (Sandoz).
200 ,, condensed water.
40 ,, formic acid.
580 ,, acid starch-tragacanth paste.
100 ,, sulphocyanide of iron 16° Tw.

1000

Brown D.R. (with chrome).

150 grms. dinitrosoresorcin 25 per cent. paste.
100 ,, potassium sulphite 70° Tw.
600 ,, starch-tragacanth paste (acid).
150 ,, acetate of chrome 25° Tw.

1000

Print, steam, and open soap at 80°–90° C.

Brown D.R. at full strength gives a fast dark cutch brown; when reduced 1 : 10, or more, pleasing shades of a warm fawn very fast to light and soap are obtained.

Dinitrosoresorcin is used chiefly as a dyestuff on iron mordants, upon which it produces fine myrtle or bluish-green shades, according as a strong or weak mordant is employed. The unprinted parts of the cloth are scarcely stained during the dyeing operation—an advantage which renders the colour particularly useful for *resist* styles.

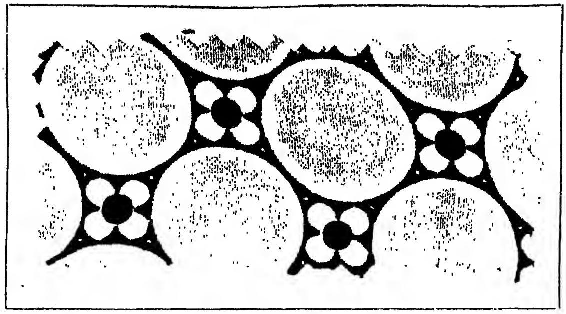
Fast Iron Green (Nitrosine N.N.) or α-nitroso-β-naphthol, is usually preferred to the above Resorcin green for printing on account of the much brighter shades it produces.

The shades it gives with iron, chrome, cobalt, and nickel are respectively bright green, brown, very rich chestnut brown, and yellow, all of which are fast to light and soap. It does not dye well on mordanted cloth, being easily decomposed by heat in aqueous solution, but it stands steaming in combination with mordants, and is therefore best adapted for and restricted to printing.

Nitrosine N.N.

50 grms. Nitrosine N.N. (powder).
180 ,, water.
670 ,, starch-tragacanth paste.
50 ,, acetic acid 9° Tw.
50 ,, pyrolignite of iron 32° Tw.

1000



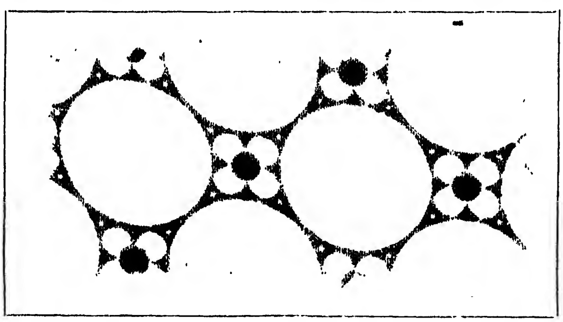
Nitrosine N.N. 5 per cent.
" " 0·625 per cent.

Brown: as green, but with acetate of chrome 32° Tw.
Chestnut: " " " acetate of cobalt 18° Tw.
Yellow: " " " acetate of nickel 16° Tw.

As in the case of Resorcin green, other salts of these metals may be employed.

The colours are fixed by a five minutes' steaming; or if printed in combination with mordant colours they are steamed an hour, followed by the usual washing and soaping.

Of the other nitroso colours, mention need only be made of *Nitrosine D.H.*, which is specially prepared to yield with chrome mordants a fuller and redder shade of brown than those ordinarily obtained from nitroso compounds. In general properties it is identical with the foregoing colours, and is applied by similar means. Only the chrome lake is of special importance.



Nitrosine D.H. (2·5 per cent. and 0·31 per cent.).

NITROSINE D.H. (5 per cent.).

50	grms.	Nitrosine D.H.
150	"	cold water.
750	"	starch-tragacanth paste.
50	"	acetate of chrome 32° Tw.
1000		

Print, steam, wash, and soap.

Lighter shades may be obtained with any of the above-mentioned colours by increasing the proportion of thickening as required.

All the Nitroso colours are readily resisted by means of hydrosulphites, and pure white reserves may be obtained under them by printing the following reserve paste.

WHITE RESERVE.

250	grms.	sulphoxylate-formaldehyde (Formosul).
400	,,	water.
300	,,	British gum.

Heat to dissolve, cool, and add—

50 grms. citrate of ammonia 40° Tw.

1000

Dry at low temperature; then over-print (cover) with, for instance, Fast iron green; dry; steam 5 minutes at 216° F.; wash and soap.

The green, brown, and yellow lakes of all the nitroso compounds are susceptible to the action of bleaching powder solutions, turning to unpleasant brown shades during the clearing operation that is frequently necessary to improve the white ground of the print. A slight addition of caustic soda to the chemic liquor overcomes this difficulty. If only about 0·5 per cent. of caustic soda is added to the ordinary clearing liquor the lakes are unaffected; with this small quantity even it is possible to use a stronger chemic than usual without harm resulting.

Application of the Natural or Vegetable Dyestuffs.

The use of these colouring matters has gradually diminished, until at the present time only about five of them find any extensive application in calico printing. These five are—Logwood, Persian berries, Quercitron bark, Catechu, and Peachwood. Others are occasionally employed in some styles of work, but, with the exception of Indigo, which is a thing apart, they belong to the past rather than to the present; and as they cannot compare in any way with their artificial competitors, they will not be dealt with here.

Logwood.—Logwood still retains its place as an important colouring matter, for the simple reason that none of the artificial blacks has so far been capable of application to all the purposes for which Logwood is adapted. Although, in many cases, Aniline black has entirely replaced Logwood, yet it cannot be printed satisfactorily with certain colouring matters, and consequently Logwood still plays an important part in the production of black-ground steam styles. Apart from its use as a black, it is a most unreliable colouring matter: in mixtures it rapidly fades, with the result that any compound shades containing it are completely transformed after a short exposure to light; and for greys, blues, and violets, with iron, chromium, tin, copper, and aluminium mordants, it is altogether out of date, not to say useless, so far as permanency is concerned.

For ordinary steam styles the black obtained with chromium mordants is the one generally preferred in practice. It is, if anything, better than a Logwood iron black, and is not so liable to affect injuriously the colours along with which it is printed, though it requires careful working to avoid this mishap. But iron blacks are altogether unsuited to printing with either Alizarin reds and pinks or basic colours; and as these enter into practically all steam styles, the Logwood iron blacks have fallen into disuse, except for a few special purposes to be noted later.

The tendency of chrome Logwood blacks to "green" is overcome by the addition of a little Alizarin, which forms a claret with chrome mordant, and their blue tone is corrected by a similar addition of the yellow colouring matter, **Quercitron bark.**

A good black for printing is made as under:—

BLACK L.

150	grms.	starch.
100	,,	British gum.
400	,,	water.
60	,,	acetic acid.
25	,,	Alizarin I.P.p. 20 per cent. (British Alizarin Co., Ltd.).
30	,,	Quercitron bark extract 48° Tw.
135	,,	Logwood extract 48° Tw.

Boil and add—

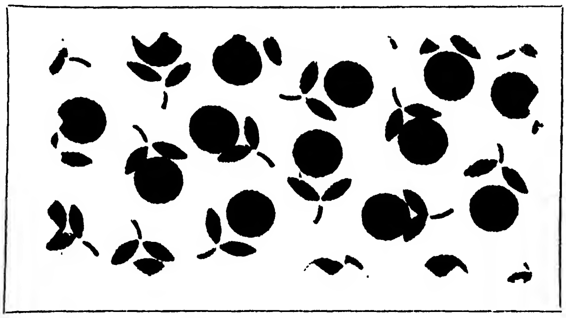
16	grms.	chlorate of soda.

Cool and add—

6	grms.	finely ground potassium ferrocyanide.
130	,,	nitrate-acetate of chrome 38° Tw.
40	,,	acetate of lime 23° Tw.

1092 = 1000 when finished.

Print and steam as usual, then wash and open soap. The chlorate of soda and yellow prussiate of potash aid in developing the black by oxidising the Logwood during the steaming process.



Steam Logwood Black.

Hematein, a dry preparation of Logwood extract, and Hemolin, a similar body, may both be used in place of Logwood. They are from two to three times stronger than Logwood extract, and must be employed accordingly.

What is known as "Fast steam black," "Carmine black," etc., is simply a reduced Logwood containing the necessary mordant. It is made by precipitating Logwood with bichromate of potash, and then treating the black lake thus obtained with bisulphite of soda. A printing colour is made from the resulting solution by merely adding the necessary quantity of thickening paste. Thus—

4 kilos. starch paste or tragacanth thickening.
1 kilo. "Fast steam black."

Fast black works very well for blotches; it does not scum so much as ordinary Logwood black, neither does it stick in the engraving so badly as a rule.

Persian Berry Extract.—This colouring matter is an extract from the dried unripe berries of various species of *Rhamnus*; it is used largely in printing for the production of steam yellow, orange, brown, and olive. The shade of yellow varies according to the mordant used.

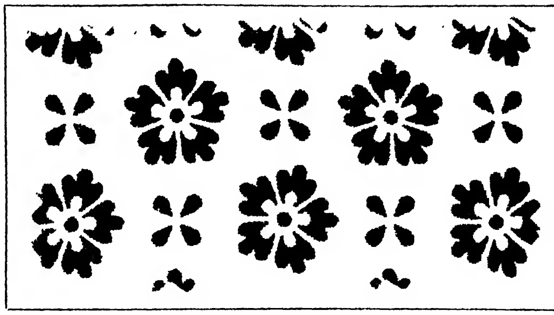
Berry Yellow I. (chrome).

120 grms. starch.
60 grms. acetic acid 9° Tw.
570 grms. water (or 530 water and 40 oil).
150 grms. Persian berry extract 48° Tw.

Boil, cool, and add—

100 grms. acetate of chrome 25° Tw.

1000



Persian Berry Yellow (Chrome).

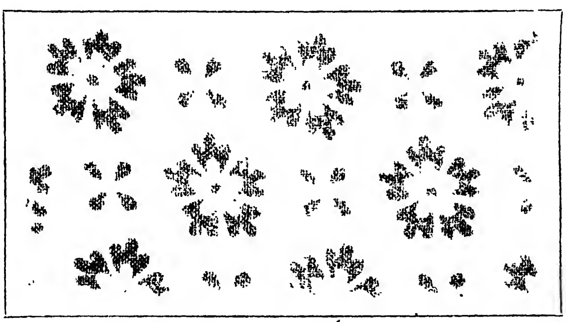
Berry Yellow II. (chrome and tin), a quiet lemon shade.

150 grms. Persian berry extract 48° Tw.
500 ,, water.
60 ,, acetic acid.
120 ,, starch.
50 ,, cotton-seed oil.

Boil, cool, and add—

90 grms. citrate of tin.
30 ,, acetate of chrome 25° Tw.

1000



Persian Berry Yellow (Alumina and Tin).

Steam Orange (Berry, Alumina, and Tin).

200 grms. Persian berry extract 48° Tw.
455 ,, water.
75 ,, acetic acid 9° Tw.
120 ,, starch.
50 ,, oil.

Boil, turn off steam, and add whilst hot—

25 grms. alum (finely ground).

Cool and add—

25 grms. acetate of soda.
50 ,, tin crystals ($SnCl_2$).

1000

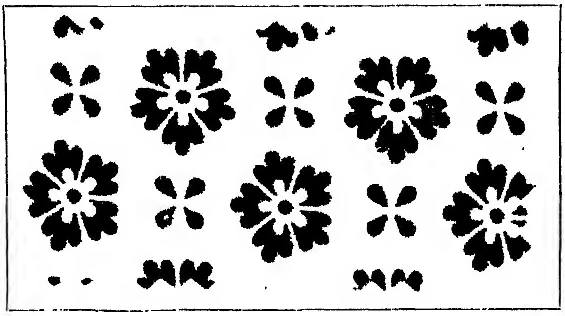
Shaded with a little Alizarin blue, Persian berry gives an old gold colour:—

OLD GOLD.

100	grms.	Persian berry extract 48° Tw.
$1\frac{1}{2}$	,,	Alizarin blue S.
825	,,	starch-tragacanth paste.
75	,,	acetate of chrome 25° Tw.
1000 (about).		

Print and steam all the above colours as usual.

Various shades of fast olives, browns, and greys are produced by mixing Persian berry yellow with Alizarin blue and Alizarin red, also fixed with chrome mordants. Similarly, a brighter range of greens and oranges, etc., is obtained by adding suitable basic colours to Persian berry yellow, which, up to a certain point, acts as a mordant for them, so that, in many cases, no addition of tannic acid is necessary.

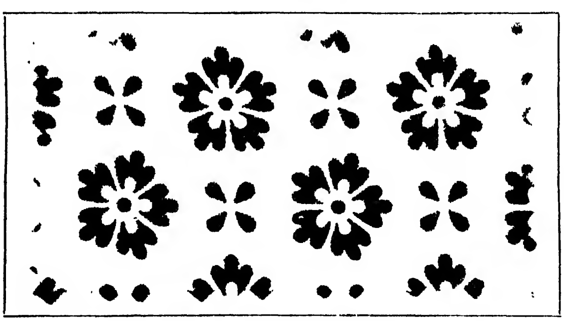


Steam Brown (Persian Berries, Alizarin, and Chrome).

STEAM BROWN.

4 parts Berry Yellow I.
1 part Claret for mixtures (*q.v.*).

Quercitron Bark Extract.—This colouring matter, usually known as "bark," is an extract from the inner bark of the *Quercus tinctoria*. Its properties, so far as calico printing is concerned, are identical with those of Persian berry extract, and it is applied in exactly the same way as the latter.



Quercitron Bark Yellow (Chrome).

The various shades of yellow and brown obtained from bark by means of chromium, aluminium, and tin mordants are yellower and duller in tone than the corresponding shades derived from Persian berries, but they are equally fast, and are quite as important.

The chief use of bark is in the making of olives and browns, for which purpose it may be mixed with any of the steam Alizarin or the basic aniline colours. The recipes given for Persian berries are equally applicable to Quercitron bark.

Peachwood.—Peachwood is a red colouring matter obtained from a species of *Cæsalpinia*. With tin mordants it gives fairly bright reds; with aluminium mordants, dull bluish reds; and with mixed aluminium and iron mordants,

a dull purple. These colours are not very fast to soap; and, with the exception of the last, none of them is of any practical value at the present time. A purple printing colour made up as follows is occasionally still employed in mixtures:—

PEACHWOOD PASTE.

450	grms.	Peachwood extract 9° Tw.
325	,,	water.
80	,,	starch.
40	,,	light British gum.
25	,,	cotton-seed oil.
Boil and add—		
5	,,	potassium ferrocyanide (finely ground).
Cool and add—		
75	,,	nitrate of alumina 25° Tw.
1000		

The above mixed with Alizarin clarets and a little Logwood black is used for steam chocolates and other cheap reddish shades such as maroons and clarets. It takes the place of part of the Alizarin, and, being much cheaper, it is more economical to use in cases where a certain amount of fastness can be dispensed with. In certain dyed styles Peachwood is still employed extensively as a cheap substitute for Alizarin.

Catechu.—Although Catechu, obtained from species of *Acacia*, *Uncaria*, and *Areca*, has been displaced to a great extent by modern artificial dyestuffs, it is still used in calico printing for steam browns and drabs, very fast to soap, light, acids, and alkalies, and in the madder dyed style for obtaining browns in combination with red, chocolate, and purple.

Acetate of chrome is the mordant chiefly used for Catechu browns, but the colour can be modified by the addition of other mordants. For example, iron salts produce a greening effect; aluminium salts give a yellowish brown; and lime salts dull the red shade of brown, given with chromium mordants, to a fine dark warm drab or fawn. In all cases the further addition of an oxidising agent—*e.g.* sodium chlorate or a copper salt—is essential to the full development of steam Catechu colours.

Catechu solutions are best thickened with gum Senegal or British gum; starch gives a stronger shade, but it is apt to gelatinise on standing, with the result that, when printed, it produces an uneven, "blebby" impression. The addition of tragacanth and oil tends to overcome this disadvantage, but it is always safer to use the above gums when blotches or large objects are to be printed in Catechu browns.

The following Catechu colours have been used on the large scale with success:—

CATECHU BROWN I. (warm chestnut shade).

750	grms.	10 per cent. Catechu solution (see below).
100	,,	starch.
70	,,	6 per cent. gum tragacanth.
20	,,	cotton-seed oil.
20	,,	sodium chlorate. Boil, cool, and add—
40	,,	acetate of chrome 32° Tw.
1000		

10 per cent. CATECHU SOLUTION.

{100 grms. Catechu in cubes.
{450 ,, acetic acid 9° Tw.
{450 ,, water.

Boil till the Catechu is dissolved, and then make up to 1000 grms. with acetic acid at 9° Tw.

CATECHU BROWN II. (warm drab shade).

600 grms. 10 per cent. Catechu solution.
240 ,, British gum.
100 ,, water.
Boil and add—
20 ,, sodium chlorate.
Cool and add—
30 ,, acetate of chrome 30° Tw.
20 ,, acetate of lime 23° Tw.

1010—boil to 1000.

CATECHU DRAB.

600 grms. 10 per cent. Catechu solution.
230 ,, British gum.
100 ,, water.
Boil and add—
20 ,, sodium chlorate.
Cool and add—
25 ,, acetate of chrome 30° Tw.
15 ,, acetate of lime 23° Tw.
10 ,, potassium ferrocyanide (powdered).

1000

CATECHU BROWN III.

600 grms. Catechu 10 per cent. solution.
240 ,, British gum.
90 ,, water.
Boil, cool, and add—
30 grms. nitrate of copper 80° Tw.
30 ,, acetate of chrome 30° Tw.
20 ,, acetate of lime 23° Tw.

1010

The above colours are printed on oiled or unoiled cloth, steamed one hour without pressure, and soaped. In the last recipe, acetate of copper may replace the nitrate ; and, if desired, any of the colours may be treated in a boiling ½ per cent. solution of bichromate of potash for their further fixation, or for the development of any lead yellow that may have been printed at the same time.

Catechu possesses the property of becoming fixed upon the fibre by a process of oxidation ; and although the shades so obtained are not very dark (unless the oxidation is completed by running through bichromate of potash), they are sufficiently fast to resist the operations of dunging and dyeing in Alizarin (madder style), and consequently they frequently appear in combination with dyed reds, etc. This particular application of Catechu will be dealt with in connection with the dyed styles.

Of the other natural dyestuffs, only a few find an occasional use at the present time. The extracts of Divi-divi, Gall Nuts, Myrobalans and a preparation called "Cutcheline" all possess a certain amount of colour which can be fixed with chrome or iron mordants. They give various shades of drab, stone, fawn, and buff, and, used with some of the Alizarin colours, quite a series of soft tones of olive, sage, and other quiet colours. The same effects, however, are for the most part obtained nowadays by the use of the faster and more reliable Anthracene brown, in conjunction with Alizarin colours suited to the purpose.

Application of Basic Colours.

The basic colours consist of salts of various (mostly colourless) organic bases. The solutions of these salts, though highly coloured, are incapable of dyeing the vegetable fibres permanently, hence the base requires to be precipitated thereon in an insoluble form. For this purpose tannic acid (or such tannins as, for instance, sumach, gall nuts, myrobalans, etc.) has been found the most generally useful, since it forms insoluble salts with the colour bases, and thus fulfils the conditions of their fixation on the cloth as coloured lakes. The tannates of the colour bases are, however, soluble to some extent in water, especially if precipitated in presence of excess of tannic acid or other acids, and therefore they are not entirely fast colours. But free tannic acid is not essential to the formation of insoluble colour lakes. The insoluble metallic tannates of antimony, tin, aluminium, zinc, and iron are equally capable of combining with the organic colour bases, and not only yield highly coloured compounds, but compounds quite insoluble in water, and practically so in soap solutions.

Upon this valuable property of metallic tannates is based the application of the basic aniline colours in calico printing.

A mixture of thickening, colouring matter, tannic acid, and organic acid (to prevent the precipitation of the dyestuff) is printed on the cloth, which is then dried and steamed. During the steaming the dyestuff and tannic acid combine to form the somewhat soluble lake, which is then rendered quite insoluble by being passed through a solution of tartar-emetic and chalk. The chalk simply serves to neutralise the acidity of the bath due to the production of acid tartrate of potash by the abstraction of the antimony by the tannic acid. In this way an insoluble double tannate of antimony and colouring matter is obtained, which is attached permanently to the fibre.

The chemical constitution of the basic dyestuffs is too complicated to be touched upon here, but particulars of their composition and properties are easily accessible in such works as *A Manual of Dyeing* by Knecht, Rawson, and Loewenthal, and other similar works on the subject. All that can be dealt with at this stage is their practical application as steam colours.

Although basic colour printing pastes are comparatively simple in composition, their preparation requires to be carefully carried out, if bright, transparent, and fast colours are to be obtained. Nothing is worse than a badly made basic colour, especially if it be thickened with starch. It is absolutely useless—can neither be printed nor rectified. Defects in basic colours are almost always attributable to one (or both) of two causes, *i.e.* (1) a shortage of organic acids, and (2) an insufficient boiling of the starch paste (if starch be used). These causes operate in the direction of promoting the formation of insoluble compounds of colouring matter, thickening and tannic acid, with the result that clean, sharp impressions of the pattern are impossible to obtain. In the absence of organic acids, or other solvents such as acetine, tannic acid precipitates at once both basic colours and most thickening materials. The

starch precipitates are, by far, the most objectionable; those with modified starches (British gums and dextrines) are less so in proportion to the degree to which they have been converted into dextrine; and those with natural gums of good quality, such, for instance, as Senegal, Arabic, Karaya, and Tragacanth, are least objectionable of all. Gums and mucilages derived from locust beans, seaweed, and the like, are totally unsuited for use with tannic acid. The precipitates of the basic colours are not in themselves so detrimental, but when combined with starch, etc., they form insoluble flocculent compound lakes, which give rise to an immense amount of trouble in printing. Colours which contain any considerable amount of these lakes stick in the engraving badly during the printing operation, and are only incompletely transferred to the cloth. The lake, which ought to be produced in the fibre of the cloth, exists already formed in the colour, and as such cannot penetrate into the body of the cloth, with the result that it merely stands on the surface, adhering to it mechanically like a pigment. Printed in this state basic colours are loose, and cannot subsequently be fixed satisfactorily by any means. Moreover, they present an unpleasing " toppy " or bronzy appearance, and are invariably irregular or mottled. Usually, too, they are dull and display a halo round the printed objects, due to the more soluble portions having run into the surrounding background. On fixing and washing, a large amount of colour is removed from the fibre and is lost; what remains is still loose and marks off, and rubs or smears badly in the wet state.

Organic acids and acetine prevent the formation of undesirable precipitates in the printing colour, and if used in sufficient quantities during its preparation none of the troubles detailed above need be expected to arise. In the case of some gum colours a suitable addition of acetic acid, tartaric acid, or acetine, followed by a gentle heating, will even effect the re-solution of precipitates that have already formed. This procedure is deprecated by some authorities as being irrational, but its usefulness and efficiency have been amply demonstrated by practical experience, and so long as a sufficiency of acid is present no detrimental effect is to be feared.

The action of tannic acid on starch and its derivatives is not entirely prevented by acids, but, in acid media, the combination takes place slowly and regularly, and the precipitate formed is in a very fine state of division and evenly distributed throughout the whole mass of the paste. In this condition basic colours thickened with starch are quite suitable for printing. For the darkest shades in object or peg printing, starch may be used alone with advantage, as it gives the deepest colours; for dark blotches it is usual to mix it with gum tragacanth (dragon), which, though an excellent thickening for basic colours, is not often used by itself because it penetrates through to the back of the cloth, and thus increases the cost of production by reason of the fact that a goodly portion of the colour is lost by being printed on the back-grey or wash-blanket. For light blotches, and other heavy patterns in light shades, the basic colours are preferably thickened with British gum, or one of the natural gums, which produce much more even and transparent colours than any starch mixture, and are much more easily removed from the fibre during subsequent operations.

In order to obtain the best results with starch, the paste must contain about 10 per cent. of acetic acid, and must be boiled until it has become more or less converted into dextrine—a point which can be recognised by its becoming thin again after the initial thickening. On cooling it thickens and has a smooth translucent appearance. A paste containing 25 per cent. tragacanth mucilage is superior in working qualities to a simple starch thickening, and is generally preferred for all purposes.

Of the acid solvents employed to retard or to prevent the premature formation of colour lakes in the printing paste, acetic acid is the most important. Acetine is a much better solvent in all respects, but its price is relatively high and restricts its application to special cases, though a small addition to any basic colour is beneficial. The somewhat inferior solvent action of acetic acid is usually augmented by the addition of citric, tartaric, formic, or ethyltartaric acid. Glycollic acid has also been suggested as a partial substitute for acetic acid. Formic acid is a cheap and powerful acid and finds considerable application in practice. It possesses but poor solvent properties, and acts as a retarder in virtue of its strong acidic character. It is an unpleasant substance to work with in quantity, and, moreover, its solvent action on copper, especially in conjunction with Methylene blue and other Thiazine colours, is liable to cause trouble.

In any case the quantity of formic acid taken ought never to exceed the minimum required to produce the required result. Its effect on the hands of the men who strain the colours is much more rapid and detrimental than that of acetic acid; and its powerful acrid fumes, which are evolved copiously during the drying of the printed pieces, produce a most irritating effect on the eyes and mucous membrane of those who work in the drying rooms.

The usual method of making up a basic colour printing paste is to add a solution of the dyestuff to a previously prepared thickening, then add the necessary amount of citric, tartaric, or other acid, and, finally, the tannic acid solution mixed with a portion of the thickening. For strong colours it is usual to boil the mixture of dyestuff and thickening in order to ensure perfect solution of the former; or alternatively the colour is made directly, *i.e.* the dry starch is mixed with water, acetic acid, and a little citric acid or tartaric acid, the colour solution added, and the whole boiled until thin; the mixture is then cooled, and the tannic acid added as above. Almost all basic colours may be boiled in this way; Auramine is an exception, and must, on no account, be heated above 70° C., as it decomposes at a higher temperature.

The amount of tannic acid, of course, varies with the dyestuff employed; and where any doubt exists as to the quantity required, it can be readily removed by making a few trials with different proportions of tannic acid to dyestuff. As a rule it will be found that the proportion is between two and two and a half parts of tannic acid to one of dyestuff, but this is by no means a general rule, and must be taken only as a basis for experiment.

In the following recipes the proportions have been determined by experiments on a works scale, and may be regarded as typical of works practice:—

STARCH PASTE B.C.

1,200	grms.	wheat starch.
4,330	,,	water.
2,500	,,	tragacanth thickening 6 per cent.
1,670	,,	acetic acid 60 per cent. (12° Tw.).
300	,,	cotton-seed oil.
10,000		

Boil for $\frac{1}{4}$–$\frac{1}{2}$ hour and cool.

REDUCING PASTE (for light shades).

700	grms.	starch paste B.C. (above).
245	,,	water.
50	,,	acetic acid 60 per cent. (12° Tw.).
5	,,	tannic-acetic solution 50 per cent.
1000		

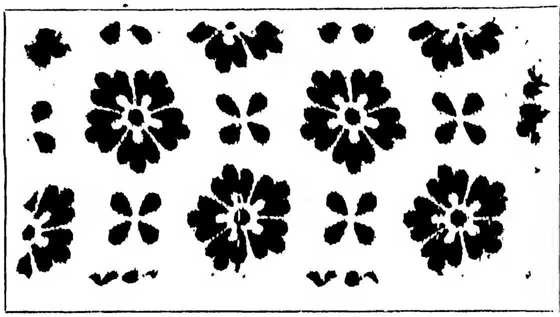
TANNIC-ACETIC SOLUTION 50 per cent.

500	grms.	tannic acid.
500	,,	acetic acid 25 per cent. (6° Tw.).
1000		

The colours are made up as follows:—

METHYLENE BLUE.

20	grms.	Methylene blue Z.F.S. (I.C.I.).
50	,,	acetic acid 40 per cent.
120	,,	water.
720	,,	starch paste B.C.



Methylene Blue Z.F.S.

Heat and add—

10 grms. tartaric acid (ground).

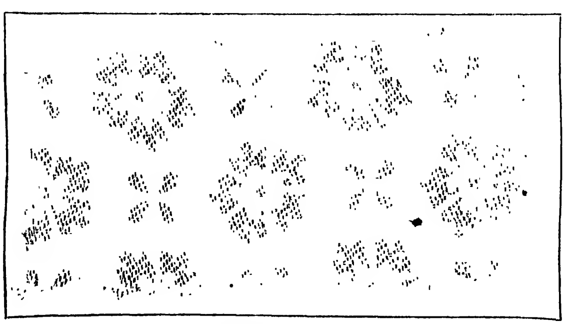
Cool and add—

80 grms. tannic-acetic solution 50 per cent.

1000

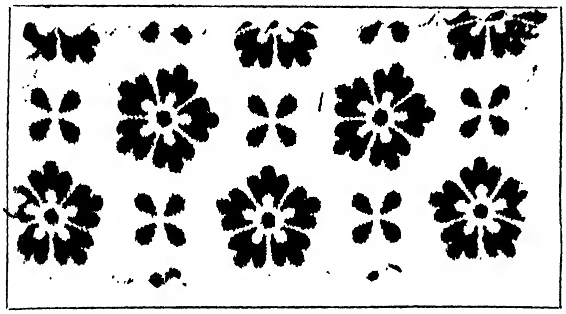
AURAMINE YELLOW.

25	grms.	Auramine O.S. (I.C.I.).
50	,,	acetic acid 40 per cent. (9° Tw.).
120	,,	water.
670	,,	starch paste B.C.
10	,,	tartaric acid.
125	,,	tannic-acetic solution 50 per cent.
1000		



Auramine O.S.

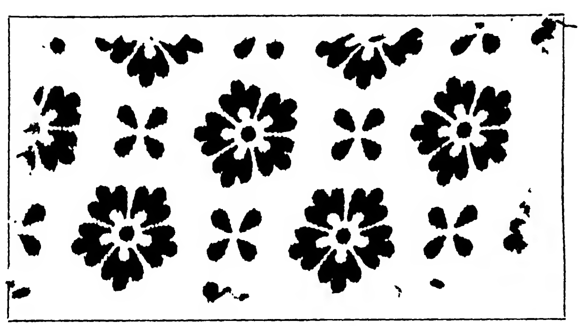
Some brands of Auramine yellow are reduced to 20 per cent. pure colour by the addition of dextrine, and these require only a little more than their own weight of tannin to fix them.



Rhodamine 6 G.D.N.S. 500 (I.C.I.).

RHODAMINE PINK.

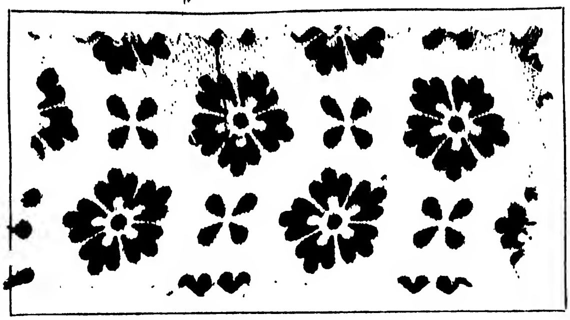
{10	grms.	Rhodamine 6 G.B.S. or 6 G.D.N.S.
{50	,,	acetic acid 9° Tw.
10	,,	tartaric acid.
100	,,	water.
630	,,	starch paste B.C.
200	,,	50 per cent. tannin-acetic solution.
1000		



Rhodamine 6 G.B.S. 500.

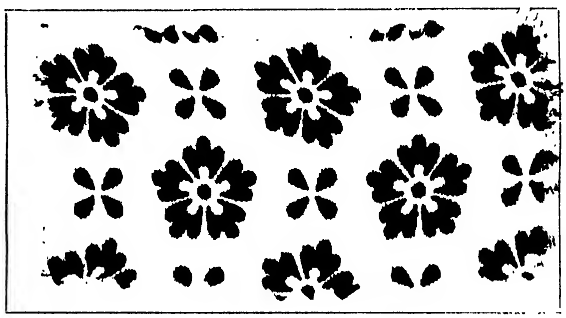
METHYL VIOLET (blue shade).

{25	grms.	Methyl violet 2 B.S. (I.C.I.).
{60	,,	acetic acid 9° Tw.
{60	,,	water.
10	,,	tartaric acid.
715	,,	starch paste.
130	,,	50 per cent. tannin-acetic solution.
1000		



Methyl Violet 2 B.S.

The red shades are prepared in exactly the same manner. Sometimes 3–4 per cent. of glycerine is added to aid the solution of the dyestuff.



Brilliant Green Y.S., with addition of $\frac{1}{8}$th of its weight of Acronol Yellow T.S.

BRILLIANT GREEN.

20	grms.	Brilliant green.
130	,,	acetic acid 9° Tw.
70	,,	water.
730	,,	starch paste.
50	,,	50 per cent. tannin-acetic solutio...
1000		

The Induline blues, which are largely used for dark navy blotches, require special treatment, as they do not dissolve easily in the ordinary solvents, and are apt to produce uneven effects if not properly prepared. For example, the colours Induline R. and B. brands in powder are best made up according to the following directions :—

INDULINE R. FOR PRINTING.

20	grms.	Induline R. powder.
60	,,	ethyltartaric acid 20° Tw.
40	,,	acetine.
50	,,	water.

Dissolve and add—

80	grms.	acetic acid 9° Tw.
600	,,	acid starch paste B.C.
150	,,	50 per cent. tannin-acetic solution.
1000		

FIXING.—After printing and steaming, all basic colours are fixed in the following bath:—

20	grms.	tartar emetic.
10	,,	chalk.
970	,,	water.
1000		

It is almost needless to say that any of the basic colours can be mixed together in any proportion to form compound shades. Such shades are, in practice, restricted to very bright colours—greens, violets, oranges—as the strength and brilliancy of the standard colours render it extremely difficult to make delicate greys, fawns, etc., twice alike. The slightest excess of pure colour alters the whole tone of the compound; and therefore, as the mode shades are very sensitive and delicately balanced, they are generally prepared from less pure primary tints.

One or other of the foregoing recipes will serve for all basic colours used as such. When they are combined with mordant dyestuffs a rather different method is adopted. Thus a very dark myrtle green is boiled as under:—

MYRTLE GREEN.

100	grms.	starch.
290	,,	water.
200	,,	5 per cent. tragacanth.
120	,,	Persian berry extract 48° Tw.
40	,,	Logwood extract 48° Tw.
Boil and add—		
20	,,	Malachite green.
100	,,	acetic acid 9° Tw.
Cool and add—		
90	,,	acetate of chrome 25° Tw.
40	,,	50 per cent. tannin-acetic solution.
1000		

The small amount of tannin used in this case is compensated for by the fact that the Persian berry acts as a mordant for basic colours, as do also most of the Alizarin colours to a certain extent.

Other Methods of Printing Basic Colours.

With the object of eliminating the final passage through tartar-emetic, which, as already noted, is essential to render basic colours reasonably fast to soaping, several suggestions have been made to incorporate the tartar-emetic with the printing colour. Under ordinary conditions this is impossible, as a precipitate at once forms, but by dissolving the antimony salt in suitable solvents satisfactory results have been obtained.

Jeanmaire observed that if salts of antimony (tartar-emetic, etc.) were dissolved in strong solutions of bleaching-powder they no longer precipitated tannic acid in the cold in the presence of organic acids. On adding such solutions to basic colour printing pastes he found that, on steaming, he obtained a fast compound lake of colour, tannic acid, and antimony, quite equal to that obtained in the usual way. This process is in use to-day and gives satisfactory prints. The colours are sufficiently bright, transparent, and fast, and render unnecessary the after-fixation in tartar-emetic. Example :—

Colour.

1000 grms. any preceding basic colour.

25 c.c. tartar-emetic solution $\frac{125}{1000}$.

Tartar-Emetic Solution $\frac{125}{1000}$.

125 grms. tartar-emetic.
875 ,, bleaching-powder solution 16° Tw.

Make up to 1000 cubic centimetres.

Resorcin also inhibits the formation of unworkable precipitates in mixtures of basic colour, tannic acid, and antimony salts, but it is not so efficient as bleaching-powder. In reality an extremely finely divided precipitate is formed which partly dissolves in steaming and penetrates fairly well into the cloth. In this state the colours find a certain limited application for small patterns, but they will not stand reduction, nor are they suited to blotch printing. Moreover, they do not keep well ; and if precipitation is to be retarded to any useful extent they must contain at least 10 per cent. resorcin and relatively large quantities of fixed organic acids (tartaric or oxalic), which, of course, are not without danger, and exclude their use for styles which require a long steaming. On the whole, the process is impracticable, and its only interest lies in the fact that it led to the introduction of a really useful and economical method of utilising the solvent properties of resorcin.

Diserens' Process.[1]—During the course of a study on the solubility of different metallic tannates, Diserens found that tannate of zinc was much more soluble in resorcin than tannate of antimony. Even in a colour containing 60–70 grms. of tannic acid and 70 grms. of resorcin per kilo. no precipitation occurred when as much as 350 grms. of zinc chloride were added. The question of using zinc salts in place of antimony salts for the fixation of basic colours had long before been under consideration without any satisfactory result being arrived at. Printed and steamed basic colours, containing tannin, when fixed in solutions of zinc chloride or sulphate were always looser to soaping and light than when fixed in tartar-emetic. Quite a different result is obtained if the zinc salt is introduced into a printing colour in which *resorcin* is employed as solvent in place of acetine or acetic acid.

No precipitation of any kind occurs ; and the colour being in solution, and not in the form of a finely divided lake, can be reduced in shade to any extent and used for any style of printing—even blotches. The shades obtained are as pure, transparent, and fast as those obtained in the usual way, and much

[1] *Revue Générale des Matières Colorantes*, Dec. 1917.

more so than those produced from colours containing tannate of antimony. Instead of resorcin, several other substances may be utilised as solvents for zinc tannate. Amongst these may be noted, phenol, gallic acid and glycollic acid ; they are not, however, so efficient as resorcin.

The printing colours are prepared as follows :—

COLOUR.

30	grms.	basic colour.
50	,,	glycerine.
75	,,	resorcin.
75	,,	water ; dissolve and add—
570	,,	gum Senegal 50 per cent. solution.
40	,,	zinc chloride.
120	,,	tannic-acetic 50 per cent.
20	,,	rape oil.
20	,,	turpentine.
1000		

Print, steam three minutes in the rapid ager, and wash off at full width. A soaping may be given if necessary. An hour's steaming may be given if the colours are associated with mordant colours.

The advantages of Diserens' process are that it eliminates the expensive after-treatment in tartar-emetic, and is cheaper and quicker in consequence; that it renders unnecessary the introduction of costly fixed organic acids (citric, tartaric) ; and, finally, that it simplifies the process by cutting out an operation and that the colours are fast and bright and free from the defects of marking-off and rubbing.

With the exception of Rhodamine B. extra, the majority of the basic colours are applicable by this method. To obtain good results, however, it is necessary to use a good quality of resorcin. A suitable sample should melt at between 117° C. and 119° C. ; its aqueous solution ought not to give any precipitate with lead acetate ; and, in the dry state, it ought not to turn brown on exposure to air.

Basic Colours Fixed with Metallic Mordants.

A few basic colours of the Rhodamine type, and occasionally Victoria blue, are printed with acetate of chrome as fixing agent or mordant. The lakes are very bright and will withstand a washing in water ; to soap and light they are comparatively loose.

Rhodamine 6 G., Rhodamine B., and Tannin pink find most employment as chrome colours, the two last in fact giving superior results with chrome than with tannin in point of colour.

Another method of fixing basic colours is based upon their property of forming insoluble compounds with arsenite of alumina. It was the only method available before the discovery of the tannic acid lakes of basic colours ; and although prohibited in most countries on account of the poisonous nature of its ingredients, it is still used to a slight extent in this country and America. As a matter of fact, the arsenic contained by the colour is in an insoluble form, and is not followed by the injurious consequences that are attributed to it by non-technical legislators.

The following formula will serve as an example of this general method of preparing basic colours for printing.

RHODAMINE PINK.

10	grms.	Rhodamine 6 G. extra.
50	,,	acetic acid 9° Tw.
100	,,	water.
750	,,	alumina paste.
90	,,	arsenic standard.
1000		

ALUMINA PASTE.

60	grms.	flour.
60	,,	starch.
850	,,	Red liquor (acetate of alumina) 8° Tw.
30	,,	cotton-seed oil.
1000		

Boil and cool.

ARSENIC STANDARD.

150	grms.	arsenious oxide (As_2O_3).
850	,,	glycerine.
1000		

Heat till dissolved ; or—

150	grms.	arsenious oxide.
150	,,	borax.
700	,,	water.
1000		

Print on oiled or unoiled cloth, steam, wash, and lightly soap. The brightest and fastest colours are produced on oiled cloth : the oil acts both as a mordant for the colouring matter and as a fixing agent for the alumina. In steaming the alumina, oil and arsenious acid combine to form an insoluble precipitate of aluminium arsenite and oleate, and this, in turn, combines with the colour base, producing an insoluble lake.

The alumina lakes of the basic colours are more brilliant than the corresponding tannin-antimony lakes, but their fastness to soap is inferior, and they are only used in those classes of work where brightness is more important commercially than fastness.

Basic colours may also be fixed mechanically with albumen, but this method is rarely employed except when they are used to modify the shade of pigment colours, and in the zinc oxide process of resisting Aniline black. The mordant dyes when fixed on the fibre may also act as mordants for basic colours. Consequently basic colours are sometimes added to mordant printing colours with the object of brightening or otherwise modifying the shade.

Amongst the fast steam colours, the basic colours fixed with tannic acid are, as a class, by far the most brilliant at the disposal of the calico printer. As regards fastness, they cannot compare with the mordant colours, although individual members of the group leave little to be desired in this respect. But they afford facilities for the production of colours that cannot be obtained in any other way, and they allow of an enormous range of shades being introduced into styles that were formerly restricted to a few colours only. They comprise all tones of red, blue, yellow, green, violet, and grey, and, as they are all applied in the same manner, they can be mixed together to form an infinite

variety of secondary and tertiary tints; so that, with their ease of application, their great tinctorial strength, their vast variety, and their adaptability to many diverse styles, the basic colours constitute one of the most important classes of substances used in calico printing.

Of the numerous basic colours now on the market the following few are perhaps the most generally useful, though it is difficult to single out the best from among so great a number of equally good products:—

Reds:—Rhodamine, Irisamine, Induline Scarlet, Magenta, Safranine.

Yellows:—Auramine, Thioflavine T., Tannin Orange, Acridine Yellow, Acridine Orange, Rhoduline Yellow, and Acronol Yellow.

Blues:—Methylene, Thionine, Cresyl, Marine, Victoria, Indoine, Indulines, and Acetinduline.

Greens:—Malachite, Brilliant, Diamond, Methylene.

Violets:—Methyl, Ethyl, Rhoduline, Cresyl.

Browns:—Bismarck, and similar products.

Greys:—Nigrosine, Methylene.

Many of the above colours are sold under different names by different makers, and most of them are made in several shades, so that almost any tone can be obtained easily without mixing.

Application of Pigment or Albumen Colours.

These colours include the highly coloured, insoluble substances, whether mineral or vegetable, that are applied to the fibre in an insoluble state. Their fixation is effected by means of a solution of albumen with which they are mixed, and which, on drying and steaming, coagulates and encloses the pigments in an insoluble envelope—fixes them on the fibre mechanically in the same way that paint is fixed on canvas by drying oils. The most important pigments are:—Chrome yellow and orange; Guignet's green (an oxide of chromium); Ultramarine blue, and its derivatives Ultramarine pink, green, and violet; Vermilion and numerous imitations and substitutes, which consist for the most part of aniline colour lakes, and even of red lead tinted with basic colours; Lampblack, and the various earths—*e.g.* siennas, umbers, ochres, etc.—and mixtures of oxide of iron with other precipitates for special shades of buff and fawn.

With varying proportions, according as to whether they are in paste or powder form, the method of making up and of applying each of the above colours is practically identical.

Pigment Red.

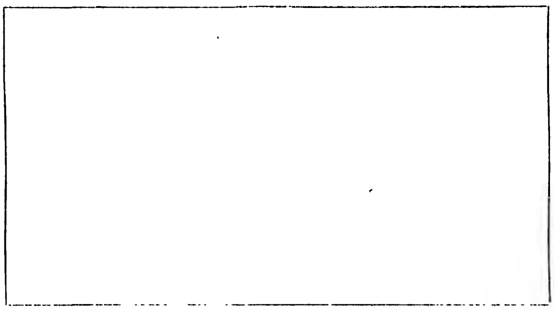
250	grms.	Vermilion.
500	,,	40 per cent. blood albumen solution.
250	,,	8 per cent. gum tragacanth.
1000		

Pigment Yellow or Orange.

300	grms.	Chrome yellow or orange.
300	,,	40 per cent. blood albumen solution.
30	,,	cotton-seed oil.
20	,,	glycerine.
30	,,	turpentine.
320	,,	6 per cent. tragacanth thickening.
1000		

PIGMENT BLUE (pink, green, or violet).

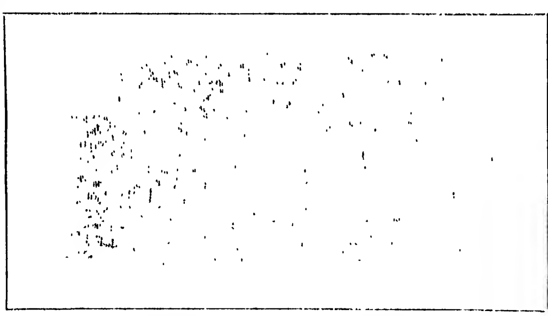
300	grms.	Ultramarine blue or pink, etc.
300	,,	40 per cent. albumen solution.
30	,,	glycerine.
20	,,	turpentine.
30	,,	oil.
10	,,	ammonia.
310	,,	6 per cent. gum tragacanth thickening.
1000		



Ultramarine Blue (British Ultramarine Co., Ltd.).

PIGMENT GREEN.

240	grms.	Guignet's green.
280	,,	40 per cent. albumen solution.
410	,,	6 per cent. tragacanth thickening.
10	,,	ammonia.
30	,,	turpentine.
30	,,	oil.
1000		

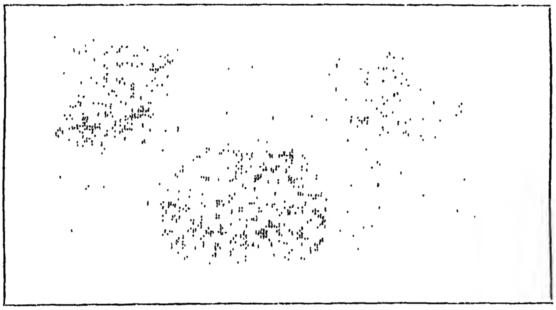


Guignet's Green (T.S. Whittle).

PIGMENT GREY.

400	grms.	lampblack.
300	,,	albumen 40 per cent. solution,
300	,,	6 per cent. gum tragacanth.
1000		

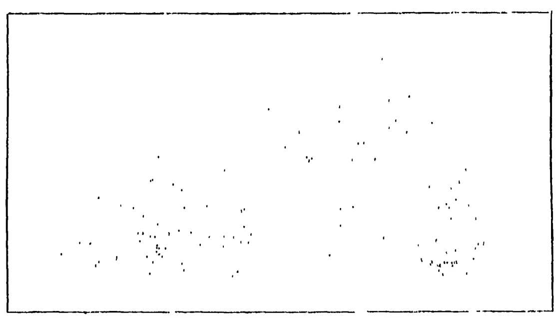
In making all pigment colours, the pigment is first thoroughly incorporated with the albumen, which is added gradually; the thickening is then added and the whole well mixed. In works where grinding mills are installed, the process can be carried out much more rapidly and perfectly than when the ingredients have to be beaten together by hand or in a colour pan. The whole of the mass can be ground until it is perfectly smooth and homogeneous.



Ultramarine Violet (British Ultramarine Co., Ltd.).

The great disadvantage of pigment colours is that they are excessively liable to froth in printing, owing to the churning action they are subjected to in the colour box. So far, nothing has been successful in entirely overcoming this difficulty, but its effect has been reduced to a minimum by the addition of various substances which do not retain air, such as benzine, turpentine, and ammonia. Oil exercises a beneficial effect in this direction, and at the same time it helps to prevent "sticking in."

In the process patented by W. E. Kay and The Calico Printers' Association, Ltd., glue or casein is made to take the place of albumen as the fixing agent. To this end the printing colour is made up of glue or of a solution of casein in borax and the pigment colour. This is printed on, and the pieces are subsequently passed through a chamber containing formaldehyde vapour, which renders the glue (or casein) insoluble in water.



Ultramarine Pink (British Ultramarine Co., Ltd.).

After printing, pigment-coloured goods are steamed for an hour; the albumen is completely coagulated during this process, and adheres firmly to the cloth, enclosing the pigments, with which it is mixed, in an insoluble envelope, and thus fixing them on the fibre.

Pigment colours fixed in this way are very fast to soaping, but being more or less attached to the surface of the cloth, they are apt to be removed by rubbing, and for this reason they are always soaped in the open soaper at full width—never in the rope state.

Sericose L.C. Extra (I.G.) is also used for thickening and fixing pigment colours—especially those white bodies, such as zinc oxide and titanium oxide, which are employed for damask effects.

The chief use of pigment colours is for the printing of shirtings, linings, and pale blotches on all sorts of cloth. Being fast to light, pale pigment blotches do not fade; but they cannot be used in cases where a lustrous finish is required all over the surface of the cloth, because they produce a dull matt surface which remains even after the most severe calendering.

In addition to direct printing, pigment colours are largely used for coloured resists under Aniline black, and for discharges on Indigo-dyed grounds.

Application of Direct Dyeing Colours.

The direct cotton colours do not find any very extended employment in steam styles, except for obtaining tinted grounds on previously printed goods. The shades they give are neither very fast nor very bright in most cases, at least not so bright as those obtained with basic colours, though brighter than all but a few of the mordant colours. They are usually printed with the addition of phosphate of soda, the slight alkalinity of which aids their penetration into the body of the cloth. If required to resist soaping, a further addition of albumen may be made, in which case they yield colours fairly fast to soap. They possess the property of becoming fixed upon the cotton fibre without the aid of any mordant, and for styles that are not required to withstand washing they are a useful class of colour to use.

The range includes all colours, and all may be applied in the same way. Some variation in the proportions is of course necessary according to the depth of shade required, but, that apart, the following formula will answer for all:—

Direct Colour Printing Paste.

$\left\{\begin{array}{l}\text{50 grms. of direct colour (Erika, etc.).}\\ \text{400 ,, boiling water.}\end{array}\right.$

520 ,, 6 per cent. tragacanth thickening.
30 ,, phosphate of soda.

1000

Heat together and cool when solution is effected. Print, steam one hour, and wash.

The Same with Albumen.

50 grms. Erika pink, Diamine sky blue, etc.
200 ,, boiling water.

Dissolve and add—

30 grms. phosphate of soda.
460 ,, 6 per cent. gum-tragacanth thickening.

Boil, cool, and add—

260 grms. 40 per cent. blood albumen solution.

1000

Print, steam, wash, and soap.

The addition of a small proportion of glycerin to the printing colour greatly facilitates (according to Justin Müller) its fixation.

The direct colours play an important part in two styles to be dealt with later—"discharges" and "crepons,"—but for ordinary steam work their employment is very limited, not to say unimportant. Some very beautiful effects may be realised by their means, but unfortunately they are not fast; and as they possess no compensating advantages, they cannot compete with or replace the faster mordant and basic colours.

Aniline Black.

Unlike other coal-tar colouring matters, Aniline black does not exist as a dyestuff ready for application, but must be produced upon the fibre itself. Neither is it wholly a steam colour, for its development, under proper conditions, can be brought about quite as easily by a mere exposure to the warm, moist atmosphere of an ageing room as by a run through a steam ager, or by a prolonged steaming in a continuous steaming apparatus.

Aniline black is in reality an oxidation product of aniline, and it is formed on the fibre by printing a thickened mixture of a soluble aniline salt, an oxidising agent, and one of several oxygen carriers, which always consist of a salt of some metal capable of existing in two states of oxidation. After printing, the cloth is dried and exposed to the action of air or steam, under the influence of which the printed parts assume, in a very short time, a dark green appearance, due to the formation of a body known as Emeraldine, an oxidation product intermediate between aniline and Aniline black proper. To convert the Emeraldine into black it is subjected to further oxidation by a run through a hot solution of bichromate of potash, which transforms it into Nigraniline, or into a still more highly oxidised body known as Ungreenable Black.

The salts of Emeraldine are green, but when treated in alkaline or soap solutions they are converted into the base which is of a deep blue colour so intense as to be virtually a black. An insufficiently oxidised black rapidly regains its original green colour when exposed to the action of the acid reducing agents so often present in the air of manufacturing districts, and for this reason it is necessary to push the oxidation of the aniline beyond the stage represented by Nigraniline. This may be done in several ways, but a run through bichromate of potash is the most generally convenient in practice, and quite satisfactory. The Nigraniline obtained by treating Emeraldine in a *cold* solution of bichromate is a very deep blue base, the salts of which are also of the same deep hue. It turns green much less readily than Emeraldine, but it is none the less very susceptible to the action of mineral acids and reducing agents, both of which re-convert it into salts of Emeraldine. Hence a *hot* solution of bichromate is always used where possible, since it exercises a more energetic oxidising action, and produces a black very fast to acids, alkalies, air, soap, and light. It is a fact well known to most practical men, that the presence of free aniline is essential to the formation of an absolutely fast ungreenable black, but until recently, it was not known whether the Nigraniline combined with a further quantity of aniline in the final reactions, or whether the aniline simply neutralised the acidity of the lower products of oxidation.[1] Neutrality certainly does promote the formation of an ungreenable black, and in conjunction with energetic oxidation at a comparatively high temperature (102° C.) it allows of a good, fast black being obtained without the necessity for a subsequent treatment in bichromate of potash.

This fact is taken advantage of in styles of printing which do not permit of *after-chroming.* A little free aniline is introduced into the printing mixture, together with an excess of some neutral oxygen carrier [$K_4Fe(CN_6)$], and these, by neutralising the acids liberated in ageing or steaming, not merely tend to the production of an ungreenable black, but also prevent, to a great extent, the tendering of the printed fabric during the process of oxidation. If these *unchromed* blacks are not quite so satisfactory, as regards their absolute resistance to greening agencies, as the *chromed* blacks, they are at least sufficiently good to outlast any of the colours with which they are associated, and which have necessitated the omission of the final chroming.

[1] See Ungreenable blacks.

Interesting as it would be to trace the development of Aniline black from its inception to the present time, it is not possible here to do more than to describe and illustrate a few typical processes that have survived the test of experience.

A complete and systematic survey of all the more important researches and suggestions relating to Aniline black will be found in *Le Noir d'Aniline*, by Noelting, Lehne, and Piquet, 1908.

Aniline blacks derived from commercial aniline oils differ considerably in shade and resistance to acids. Pure aniline yields a fine blue-black of great richness and beauty, which is, however, the most liable of all to the defect of greening; mixtures of aniline with its homologues, the toluidines and xylidines, give denser and more neutral shades of black which vary in tone according to the relative proportions of the various constituents of the mixture. Ortho-toluidine produces a violet-black, little inferior to that obtained from pure aniline and much less liable to turn green. The para- and meta-toluidines give brown shades, and commercial xylidines reddish-brown shades, of black which, though of no importance as colours, are useful for modifying the tone of an aniline black and, by reason of their greater resistance to greening influences, of imparting greater permanency to it. For these reasons an impure aniline is preferred in practice—a mixture containing 25 per cent. of meta-toluidine being perhaps the best.

Ungreenable blacks, properly speaking, are of comparatively recent introduction; and, for convenience, they are dealt with at the end of this section.

An Aniline black printing colour consists of three distinct parts: (1) a soluble salt of aniline, (2) an oxidising agent, and (3) an oxygen carrier. The aniline salt employed is generally the hydrochloride, though the tartrate, chlorate, nitrate, and other salts are occasionally used for special purposes. The only oxidising agent used in practice is chlorate of soda. It comes into the market in a state of great purity, and is generally preferred on account of its cheapness and solubility—two qualities which render it more economical and efficient than chlorate of potash. The oxygen carriers, on the other hand, are more numerous, but, as a rule, only about four find any extended application, namely, copper sulphide, copper sulphocyanide, vanadium chloride, and yellow prussiate of potash. The blacks produced by means of the latter salts are designated respectively Copper sulphide black, Copper sulphocyanide black, Vanadium black, and Prussiate black. These four, together with a fifth known as Chromate black from the quantity of chromate of lead it contains, are the only blacks, out of the scores of oxidation blacks that have been proposed from time to time, that have attained to any degree of permanent success. All the others are obsolete, and, with the exception of Green's recently patented process and Diphenyl black, the above compounds hold undisputed sway in practice.

(1) Copper Sulphide Black.—The introduction of copper sulphide as an oxygen carrier was due to Charles Lauth in 1864.

The Copper sulphide black is by no means an easily worked colour; it is always liable to attack the doctors if the latter are not varnished, and even then their edges are more or less rapidly affected, so that they require constant attention and re-sharpening to keep them in working condition. But, all things considered, it is a valuable colour, and if carefully prepared and worked as cold as possible the oxidation of the sulphide to sulphate in the printing paste may be reduced to a minimum, and the quality of the doctor edge be preserved accordingly. The great disadvantage of sulphide of copper is that it is extremely apt to stick in the engraving, no matter how carefully the colour may have been prepared, and therefore it is always replaced by Prussiate or

Vanadium blacks (which contain no insoluble matter) whenever the style of work permits.

An excess of free aniline is always allowed in Copper sulphide blacks to overcome the tendering of the fibre, and to promote the formation of ungreenable black in the chroming process. A little ammonium chloride is also frequently added to aid in the reactions. The following is a black in actual use:—

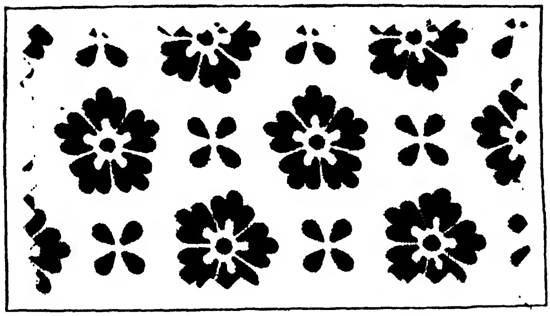
COPPER SULPHIDE BLACK.

150 grms. starch.
80 ,, British gum.
528 ,, water.
40 ,, chlorate of soda.
35 grms. oil (cotton-seed).
5 grms. Methyl violet (to sighten the colour).

Boil, cool, and add—

95 grms. aniline salt (hydrochloride).
17 grms. aniline oil.
50 grms. sulphide of copper (30 per cent. paste).

1000



Aniline Black (Copper Sulphide).

Print on white cloth, dry, and pass for three minutes through the rapid ager at not above 65° C. If desired, the development of the black may be more slowly but quite as well effected by hanging the printed goods in an ageing room for 10–24 hours. This method is adopted when the black is printed along with aluminium or iron mordants, and it develops very well at the temperature of a cool chamber 55°–60° C.

Ordinary goods, after ageing or steaming for three minutes, are afterwards chromed in a hot solution of bichromate of potash (1 per cent.).

(2) COPPER SULPHOCYANIDE BLACK.—The use of cuprous sulphocyanide as an oxygen carrier was patented by Higgin in 1868. Blacks made according to Higgin's process oxidise more slowly than sulphide of copper blacks, and they withstand a longer steaming, besides which they work a good deal better in printing. It is surprising, therefore, that they are not used more, but for some reason they appear to have fallen into disfavour.

CUPROUS SULPHOCYANIDE BLACK.

150 grms. starch.
90 ,, British gum.
530 ,, water.
20 ,, oil.
40 ,, chlorate of soda.

Boil, cool, and add—

$\left\{\begin{array}{l}\text{25 grms. ammonium chloride.}\\ \text{20 ,, water.}\end{array}\right.$
80 ,, aniline salt.
20 ,, aniline oil.
25 ,, cuprous sulphocyanide paste ("white paste").

1000

Print, dry, and either age, pass through the rapid ager, or steam fifteen minutes, chrome and soap.

If printed with colours that require an hour's steaming, the cloth, after the development of the black, must be passed through an atmosphere of ammonia before being subjected to the prolonged action of hot steam. This applies to all aniline blacks printed with steam colours.

Higgin's black is frequently combined with the Chromate black of Schmidlin.

(3) Vanadium Black.—The researches of Lightfoot and of G. Witz and A. Guyard resulted in the introduction of vanadium salts as oxygen carriers. In presence of the requisite quantity of chlorate of soda, one part of vanadium is sufficient to convert two thousand parts of aniline into black. Metavanadate of ammonia was at first used, but H. Schmid showed that the chloride is better, and in practice the latter salt is always used. A recipe for its preparation has already been given.

Metavanadate of lead[1] has been proposed as an oxygen carrier in place of the soluble vanadium chloride, with the object of increasing the stability of the printing colour. It is readily prepared by adding lead acetate to a solution of vanadium chloride until the blue colour of the latter disappears. Prepared in this way it contains lead chloride which has, however, no detrimental influence on the ultimate black. Metavanadate of lead certainly improves the stability of aniline black printing pastes, but it has not hitherto been introduced into practice on any considerable scale.

The amount of vanadium used varies according to the class of work in hand; 3 grammes of 1 per cent. solution of the chloride per kilogramme of printing colour is about the average, but for fine patterns which allow of oxidation at a higher temperature 5 grammes is a usual quantity to employ.

As Vanadium blacks contain no solid matter, they print much better than either of the preceding or the chromate of lead blacks; but, on the other hand, they oxidise more rapidly; and as the black already formed in the colour before printing would only adhere mechanically to the cloth and would be washed off in soaping, it is of the utmost importance only to add the vanadium chloride to the colour immediately before use.

Apart from its good working qualities, Vanadium black is exceptionally well adapted for printing along with steam Alizarin reds and pinks. The mere trace of metallic vanadium which it contains has no effect on the Alizarin colours, and if it is printed in lightly engraved patterns it may be steamed with safety after a run through ammonia vapour subsequent to its development by ageing in the rapid ager. The following recipe has given good results on the large scale:—

Vanadium Black.

100	grms.	starch.
80	„	British gum.
550	„	water.
40	„	chlorate of soda.
20	„	cotton-seed oil.

Boil, cool, and add cold—

90	grms.	aniline salt.
20	„	aniline oil.
{ 5	„	1 per cent. vanadium chloride solution.
{ 95	„	water.
1000		after boiling.

[1] G. Friedlaender, *Rév. gén. des Matières Colorantes.* 1909.

After printing and drying, the above black is developed by running through the rapid ager—2 minutes at 80°–90° C.—or it may be hung in an ageing room at 32°–36° C. until it has become quite black, after which it may be chromed. If developed by a short passage through the ager at a high temperature (95° C.) it is not necessary to chrome it; but, of course, all aniline blacks are improved by chroming, and therefore it is not to be omitted unless it destroys the other colours printed along with the black.

Vanadium and copper sulphide, or ferrocyanide of potash, are sometimes used together to form mixed blacks, but it is doubtful whether any advantage is derived from this procedure unless it be that in the case of the ferrocyanide a certain amount of Prussian blue is formed which modifies the shade. If the blue is intended to act in this way the printed goods must not be soaped after chroming, but passed through a chalk bath at 60° C. and then well washed in hot water.

(4) Prussiate Black.—Prussiate black was invented by Lightfoot in 1863, and was patented by him in July of that year, five months before Cordillot applied for a patent for a similar black. For ordinary printing the following black yields excellent results:—

100 grms. starch.
20 „ British gum.
61 „ potassium ferrocyanide.
707 „ water.

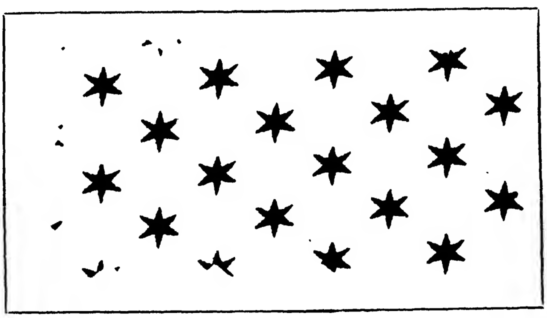
Boil, turn off steam, and add—

28 grms. chlorate of soda.

Cool and add—

84 „ aniline salt (which dissolves in the cold).

After printing, this black is developed by a run of four minutes through the rapid ager at, at least, for the best colour, 95° C. If it be now passed through the vapour of ammonia it may be steamed with perfect safety for about an hour in the continuous steamer—an advantage which allows of it being used in conjunction with a large number of steam colours. Although it contains a large amount of iron, it can be employed successfully with steam Alizarin reds and pinks if printed with care, and by interposing a *starch roller* between the black and pink or red rollers.



Aniline Black (Prussiate).

For black and white effects Prussiate black is merely developed by running the goods through the rapid ager followed by a chroming and soaping. Prolonged steaming is only employed when it is required for ordinary steam colours printed in combination with the black; it is not by any means necessary to the development of the black, although it improves its shade in some respects, and certainly makes it more resistant to the greening action of acids and reducing agents.

If ferrocyanide of ammonia be used in place of the potash salt, and a

sufficient quantity is employed to neutralise the mineral acids liberated in steaming, it is quite possible to obtain a black that is practically ungreenable without any after-treatment with bichromate of potash. The printing colour, however, does not keep very long, and must be used at once. Curiously enough, too, sodium ferrocyanide has a similar effect in accelerating the decomposition of the printing colour. Why this should be is not satisfactorily explained, but it is a well-known fact in practice, and has prevented the use of the sodium salt for printing, though it is occasionally used in the dyeing of plain blacks.

The chief advantages of the Prussiate (potash) blacks are that they have practically no tendering action on the fibre, that they work as well as any other colour in printing, and that they keep well for two or three days if stored in a cool place. They are more expensive to produce than the preceding blacks, and do not yield quite the same shades, but these are minor points in comparison with their facility of application, etc., and, at the present time, it is safe to say that Prussiate blacks are more largely used in printing than any other.

(5) Chromate Black.—This black was invented by J. Schmidlin, and can be used as a steam colour in the ordinary way, since, under proper conditions, it has no action on the cotton fibre. It consists of aniline salt, chlorate of soda, and chromate of lead, with occasionally an addition of ammonium chloride. The lead chromate plays the double rôle of an oxidising agent and a neutralising agent. As a rule a copper salt is added when the rate of development requires to be accelerated.

Chromate Black I.

80 grms. starch.
595 ,, water.
100 ,, Chrome yellow 40 per cent. paste.

Boil and add—

100 ,, ammonium chloride.

Cool a little and add—

25 grms. chlorate of soda.

Cool completely and add—

95 grms. aniline salt.
5 ,, aniline oil.

1000

The printed goods are steamed for fifteen to twenty minutes without pressure, and then washed and soaped. No chroming is necessary.

Chromate Black II.

60 grms. starch.
590 ,, water.
100 ,, lead chromate 40 per cent. paste.

Cool a little and add—

25 grms. chlorate of soda.

Cool completely and add—

100 grms. aniline salt.
25 ,, copper sulphide 30 per cent. paste.

Print, steam fifteen minutes, wash and soap. If the black is in combination with steam colours, pass the goods through ammonia vapour after the first steaming, and then further steam for an hour. Chromate and sulphocyanide of copper blacks are frequently mixed together for steam work, and give a more brilliant black than the chromate alone, which at best only produces a black of a dull bronzy tone.

The large quantity of solid matter in Chromate blacks tends to make them work badly, but when carefully prepared they are especially suited to the printing of fine designs in which a crisp definition is essential, and, as they require no subsequent chroming, they lend themselves to a greater variety of styles than other aniline blacks.

An addition of a small proportion of *paraphenylenediamine* to all Aniline black colours has the effect of rendering them less liable to turn green. The use of this base (first proposed by P. Monnet in connection with dyed blacks) renders Aniline black so resistant to the action of sulphurous and other acids that it retains its colour under conditions that would utterly ruin any ordinary black. For printing purposes the following recipe will be found to yield a colour which is practically ungreenable and suitable for most styles of direct printing :—

Aniline Black with Paraphenylenediamine.

1023	grms.	Aniline oil.
550	,,	hydrochloric acid 33° Tw.
600	,,	acetic acid 80 per cent.
7000	,,	water.
1300	,,	starch.
500	,,	colour oil.

Boil, turn off steam, and add—

75	grms.	Paraphenylenediamine.
100	,,	hydrochloric acid 33° Tw.

Cool and add—

700	,,	chlorate of soda.
900	,,	water.
500	,,	copper sulphide 25 per cent. paste.

To 11 litres.

Print, age 3 minutes, chrome, wash, and soap.

The above is intended for finely engraved patterns. For heavier patterns it may be reduced; if reduced to about 13½ litres (13·66) it contains 75 grms. of aniline per litre. To obtain the best results it is essential to age energetically and with a good volume of steam; the presence of air also is a decided advantage.

A black made up with chlorate of aniline and sulphide of copper is at times used for certain styles; and a modification of Koechlin's tartrate of aniline black is also employed occasionally in steam work, though rarely at present.

Chlorate of Aniline.

450	grms.	chlorate of barium.
300	,,	aluminium sulphate.
1500	,,	water.

Heat to boil, and, after complete precipitation, cool to 40° C. and add—

470 grms. aniline oil.

Stir well and use the filtrate, which is a solution of aniline chlorate.

The printing paste is made as under :—

850	grms.	chlorate of aniline solution.
100	,,	starch.

Boil, cool, and add—

50 grms. 25 per cent. copper sulphide paste.

Print, and develop as for sulphide of copper black.

Koechlin's Black.—In this black, invented by Camille Koechlin, the

hydrochloride of aniline is replaced by the tartrate; in other respects it is a copper sulphide black, and is used in the same way. In practice the tartrate is made directly during the preparation of the printing colour:—

60 grms. starch.
90 „ British gum.
520 „ water.
60 „ ammonium chloride.
90 „ aniline oil.

Boil and add—

40 „ chlorate of soda.

Cool, and when cold add—

90 grms. tartaric acid (finely powdered).

And when quite dissolved add—

50 grms. sulphide of copper 30 per cent.

1000

Print, age, and chrome. The black does not develop very rapidly, and after passing through the rapid ager it is advisable to hang the goods in an ageing chamber for twenty-four hours. Tartrate of aniline is not capable of yielding a black, but under the influence of heat and moisture a double decomposition takes place between the ammonium chloride and the tartrate, and aniline hydrochloride is produced on the fibre, and is gradually oxidised to black. The best results are obtained by a slow, gentle oxidation in an ageing chamber at a temperature of 70°–80° F.

Koechlin's black may be regarded as obsolete. It is rarely or never used nowadays, and must always be chromed to produce anything like a passable black. The conditions of Aniline-black printing are now generally understood, and there is no longer any necessity to employ expensive salts like tartrate of aniline to avoid tendering the fibre. At the time of its introduction it was the only black that did not attack the fibre to an injurious extent, but at the present time the value of the cheaper aged blacks is sufficiently proved by the fact that they are still used every day in enormous quantities, while the tartrate black is now of scientific interest only.

In all cases where any Aniline black is printed on oiled cloth the proportion of aniline salt and chlorate of soda should be increased, and no aniline oil should be used. If these precautions are neglected it is impossible to obtain a good black, as the oil acts as a resist.

In many styles Aniline black has completely displaced Logwood, but the latter still maintains its importance as a steam colour by reason of its mode of fixation, which is identical with that of other steam colours. Moreover, a great number of steam colours are destroyed by the fumes of acid and aniline that are evolved during the steaming process; so that, although the Prussiate and Chromate blacks may be steamed for at least half an hour, they cannot be substituted indiscriminately for Logwood. Olives containing Methylene blue come out a dirty yellow, due to the destruction of the blue element; pale Alizarin pinks are turned yellow, owing to the acid vapours preventing the Alizarin from combining with the alumina; and even strong reds are not infrequently affected in the same way to a less degree. These defects may be remedied to some extent by passing the goods through ammonia vapour, after the black has been developed in the rapid ager,—indeed, this should always be done. If they are acted upon after this "gassing," as it is termed, they may be improved somewhat by gassing again and re-steaming, but, as a rule, it is only the strongest colours that are improved by this extra treatment, the paler ones being irretrievably spoiled. These remarks apply more especi-

ally to cases where heavy masses or blotches of black are printed; where only small objects or outlines are printed the black suffers more frequently than the colours, which, nine times out of ten, are as good as when Logwood is used.

Other applications of Aniline black will be given in treating of other styles of printing.

DIPHENYL BLACK.—This black, patented in 1901 by the Farbwerke, Meister, Lucius, & Brüning, is in some respects similar to Aniline black. It consists of the oxidation products of various amines, but, unlike Aniline black, it neither tenders the fibre nor does it turn green, and it can be steamed for an hour with perfect safety, and without in any way impoverishing the surrounding colours.

Diphenyl black comes into the market as *Diphenyl black base* and *Diphenyl black oil D.O.*, both of which are used for printing—the former for steam styles of the most delicate description, and the latter for the more ordinary black and white effects.

The oxidising agent used in most cases is chlorate of soda; aluminium chlorate may also be used, but it is not so convenient. As oxygen carriers the salts of copper are the best. Ferrocyanide of potassium throws the base out of solution, and vanadium salts act too rapidly. Cerium chloride is also a good oxygen carrier, and is employed along with sulphide of copper. Other additions are lactic acid, aluminium chloride, and the necessary thickening materials.

After printing, the goods are aged in the steam ager for 1–3 minutes, then steamed for an hour or more, if printed in Alizarin or basic colours, and finally washed and soaped in a slightly alkaline bath. Chroming is to be avoided, as it imparts an unpleasing brown tone to the black, which is, moreover, ungreenable without any such extra oxidation.

Diphenyl base and oil are soluble in acetic acid or acetin. The oil D.O. is in reality a solution of p-amidodiphenylamine in aniline; the base is p-amidodiphenylamine alone. The solution of these bodies in the ordinary acids is possible, but the salts formed are too insoluble to be employed in printing.

A good many recipes are available for the production of Diphenyl black, but the following, given by the patentees, will serve as types of those used in the majority of cases:—

DIPHENYL BLACK I.

1100	grms.	starch.
4500	,,	water.
1080	,,	acetic acid 9° Tw.
200	,,	olive oil.

Boil, turn off steam, and add—

300	grms.	chlorate of soda.

Cool and add a solution of—

350	grms.	Diphenyl black base I.
1300	,,	acetic acid 9° Tw.
450	,,	lactic acid 50 per cent.

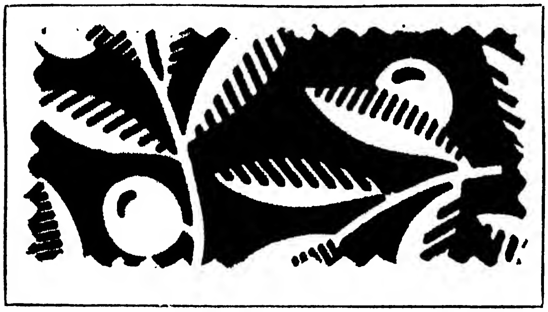
For use, further add—

100	grms.	copper sulphide 30 per cent. paste.
300	,,	water.
180	,,	aluminium chloride 52° Tw.
140	,,	cerium chloride 84° Tw.
10,000		

This black may be used with Alizarin and basic aniline colours. After printing it is a light grey and must not be overdried. It is fully developed

by a two or three minutes' passage through the rapid ager at as high a temperature as possible. Then, if the patterns contain steam colours, the goods are further steamed for 1–1½ hours, with or without pressure, fixed in tartar emetic for the basic colours, and finally soaped.

For ordinary work (single blacks and styles commonly associated with Aniline black) the following recipe containing aniline may be recommended:—



Diphenyl Black.

Diphenyl Black II.

1100	grms.	starch.
5315	,,	water.
1125	,,	acetic acid 9° Tw.
200	,,	olive oil.

Boil, cool a little, and add—

300	grms.	chlorate of soda.

Cool and add—

225	,,	lactic acid 50 per cent.
123	,,	hydrochloric acid 28° Tw.
67	,,	water.
500	,,	Diphenyl black oil D.O.

For use add—

200	,,	copper sulphide 30 per cent.
630	,,	water.
215	,,	aluminium chloride 52° Tw.
10,000		

Print on unoiled cloth, dry gently, age 2–3 minutes at 95° C., and then pass at once into an alkaline soap solution at 60°–80° C.; or if printed with Iron buff, through a hot solution of caustic soda.

As compared with Aniline blacks, the blacks obtained from *Diphenyl Black Base I.* are more expensive, but, at the same time, they are absolutely ungreenable; and as they neither give off any injurious acid vapours or gases during steaming nor require any after-treatment with bichromate of potash for their proper development, they do not either tender the fibre or destroy any of the colours with which they may be associated.

On the other hand, *Diphenyl Black Oil D.O.* can be used in place of aniline with advantage, for although its initial cost is greater, a good black can be obtained with as little as 4 per cent. (on the weight of printing colour), whereas at least 8 per cent. of aniline salt is required to produce an equally full shade, and, as a rule, not less than 9 per cent. is used.

Diphenyl Black Oil D.O., containing as it does a certain amount of aniline, possesses properties intermediate between those of pure aniline and pure Diphenyl Black Base I.; so that, as regards resistance to greening influences, it is superior to aniline. Its effect on sensitive steam colours is also much

less pronounced, since, in a black prepared from Diphenyl oil D.O., the content of mineral acid is greatly reduced, and no metallic salts, capable of forming dull compounds with the other colours, are used in sufficient quantity to act injuriously. Aniline blacks are certainly simpler in composition, and are more easily and rapidly prepared. If anything, too, they are more regular in action, and are always preferred for finely engraved patterns, when it is possible to use them, not only on account of their cheapness, but because, hitherto, they appear to be more reliable in action, and to yield fuller and deeper blacks. For fine patterns, the strength of the Diphenyl blacks almost invariably requires to be increased, and this makes them more expensive for many of the cheaper "black-cover" styles.

Taken altogether, Diphenyl blacks are superior to Aniline blacks for general steam work, and they certainly give the finest all-round *fast* black on cloth prepared in naphtholate of soda for the dyeing of Azoic colours like paranitraniline, etc. For this purpose Aniline black, pure and simple, is useless. It is probable, therefore, that Diphenyl blacks will replace both Logwood and aniline for most steam styles; but, owing to the fact that they are turned brown by bichromate of potash, it is not likely that aniline will lose any of its importance in the production of those styles which depend upon chroming for the development of their colours—*e.g.* Chrome yellow, steam Prussian blue, Endler's manganese brown, Catechu, etc., all of which are at present used in combination with Aniline black.

A. G. Green's Aniline Black.—In 1907 A. G. Green patented a process for the production of Aniline black, in which the use of an oxidising agent in the black mixture is entirely dispensed with. His process is based upon the fact, first observed by him, that aniline, in presence of an oxygen carrier and a small percentage of a para-diamine or a para-amido-phenol, is easily oxidised to Emeraldine by mere exposure to air. Moreover, by this new process it is possible to effect the oxidation of aniline in the basic state; so that the chief cause of tendering—*i.e.* the action of the mineral acids liberated during ageing—is entirely overcome, with the result that the original strength of the fabric remains unimpaired, and an ungreenable black is obtained. It is not even necessary to use a mineral acid at all, as the formation of the black is effected quite as well, if perhaps a little more slowly, in the presence of organic acids alone. Mineral acids are cheaper, however; and as it is not essential that they should be present in excess, as is necessary in ordinary Aniline blacks, they can be used with advantage, either alone or in combination with an organic acid. Formic acid is recommended by the inventor.

The most efficient oxygen carrier has been found to be cuprous chloride. Being a lower oxidised salt than the cupric chloride, it does not act upon the aniline so readily, and consequently the decomposition of the black mixture is retarded to such an extent that it remains clear and serviceable for a considerable time. In practice, the cupric salt ($CuCl_2$) is first added to the mixture, and is then reduced to cuprous chloride (Cu_2Cl_2) by the further addition of the requisite quantity of sodium meta-bisulphite, together with an amount of ammonium chloride sufficient to keep the copper salt in solution.

The application of A. G. Green's process is identical with that of the older processes, and the cloth, after printing or padding, is treated in the usual way. The black may be developed either by hanging in a warm, moist atmosphere, or by a passage through the rapid ager, or by a more prolonged steaming. It is then chromed or not as required, and finally washed and soaped.

For the dyeing of plain blacks, the process is already in use; but it has not yet found any extended application in printing, though there does not appear to be any reason for its neglect in this direction, unless it be that the

published proportions of ingredients are not suited to printing. Certainly a printing colour containing less than 2½ per cent. of aniline is not likely to yield a black, but on the small scale a fairly good result was obtained with the following colour:—

690	grms.	thick starch-tragacanth paste.
130	„	ammonium chloride.
Warm together, and, after cooling a little, add—		
50	grms.	copper chloride ($CuCl_2.2H_2O$).
15	„	meta-bisulphite of soda.
Cool and add—		
60	„	aniline oil.
4	„	paraphenylenediamine.
30	„	hydrochloric acid 30 per cent.
21	„	formic acid 90 per cent.
1000		

The above was printed on white cloth, aged three minutes at 95° C. The black was not quite satisfactory on emerging from the ager, but after an exposure of twelve hours to a moist atmosphere, followed by a hot chroming, it improved considerably, and would doubtless have been better for a more prolonged exposure to the air. Probably, too, a slightly larger quantity of mineral acid would accelerate the oxidation without attacking the fibre. Working on the above lines, good results ought to be possible of attainment; it ought to require a few experiments only to arrive at the correct proportions.

The following advantages are claimed for the process of air oxidation blacks:—(1) that they are more economical than the older blacks, owing to a more complete utilisation of the aniline; (2) that they do not attack the fibre; (3) that they are more stable than any other Aniline black mixtures, owing to the absence of energetic oxidising agents; (4) that the rate of production is increased; and (5) that the absence of noxious vapours removes all risk of injury to the health of the workmen.

Ungreenable Aniline Blacks.

The Aniline black processes described in the preceding pages are all, with the exception of the last two, liable to yield colours which are susceptible to the greening action of acids and acid-reducing agents such as sulphur dioxide, etc. The ungreenable qualities of Diphenyl black are counterbalanced by its expense, and it is not always capable of replacing Aniline black; and Green's black has not, so far, been applied with any degree of success in printing; hence the desirability of producing a printing black from aniline, and its homologues, which shall be cheaper than the first and as unalterable as the second, of all-round usefulness and of easy application by the means and plant in current use.

It is true that occasionally some of the older formulæ gave ungreenable blacks, especially when the prints were carefully aged at a low temperature, or by hanging in the air, and subsequently chromed; but the results were by no means certain, nor were the conditions under which they were obtained at all clearly understood until comparatively recently.

Notwithstanding that, during the long period that has elapsed since Aniline black was first introduced into practice (1863), many valuable improvements have been effected in its application, and certain factors essential to success have been definitely, if empirically, established, no satisfactory explanation of its actual mode of formation had ever been offered until Professor A. G.

Green published, in 1912, an account of his researches on the "Constitution of Aniline Black"—researches as important from a practical as from a scientific point of view.

In the course of these investigations,[1] A. G. Green and his collaborators established the fact that what is commonly regarded as Aniline black is merely an incompletely formed black, consisting of a mixture of Aniline black with varying proportions of its intermediate products, emeraldine and nigraniline, or even of these intermediates alone. They showed that when salts of aniline are oxidised in acid solution (as was the case with all aniline blacks then used for printing), the primary products are invariably emeraldine and/or nigraniline; and that if the oxidation be carried farther under the same conditions it leads first to pernigraniline, and finally to quinone, but not to Aniline black, as might be expected. The acid oxidation of aniline takes place in five stages, the first resulting from a condensation of eight molecules of aniline, whereby a colourless base is obtained to which the name of leucemeraldine has been given; then follow in turn protoemeraldine (violet base; yellowish green salts), emeraldine (violet base; green salts), nigraniline (dark blue base; blue salts), and pernigraniline (purple base; purple salts), which represent progressive stages in the oxidation of leucemeraldine, by direct quinonoid addition, and correspond respectively to the mono-, di-, tri-, and tetra-quinonoid stages. None of these bodies, nor any mixture of them, can be regarded as Aniline black proper, though emeraldine and nigraniline, and especially the latter, generally constitute the greater part of commercial blacks. On the contrary, they are only intermediate products in the formation of *true ungreenable black* and differ radically from it in colour, constitution, and properties. They possess an indamine-like structure, and are readily interconvertible, nigraniline being instantly reduced to emeraldine or proto-emeraldine, both of which are green, by sulphurous acid. On the other hand, Aniline black is an azonium derivative, and, on treatment with sulphurous acid, it yields a brown leuco compound which re-oxidises to the original shade of black on exposure to the air, whereas emeraldine retains its green colour; it is also a black base and forms black salts. From the foregoing it is evident that the cause of the "greening" of some Aniline blacks is due to the fact that they contain, or perhaps consist entirely of, intermediate products.

It has long been recognised, in practice, that ordinary Aniline blacks can only be rendered ungreenable by chroming them in presence of free aniline under as neutral conditions as possible. A study of the reactions involved in this process led Green (1909) to advance the view that the formation of Aniline black is not due to oxidation alone, but also to a condensation of nigraniline with a further quantity of aniline. He showed that one molecular proportion of nigraniline may combine with one, two, or three molecular proportions of aniline, forming mono-, di-, and triphenylated Aniline blacks, of which the last alone is ungreenable, and corresponds to the true ungreenable Aniline black produced on the fibre by the bichromate process of dyeing. The fact that neutral, or only feebly acid, conditions are essential to the formation of the condensation products confirms the older observation noted above.

During the conversion of nigraniline into Aniline black an intermolecular re-arrangement takes place, the indamine or para-quinonoid structure of the former being transformed into the azine or ortho-quinonoid structure of the latter as indicated clearly by the difference in their behaviour towards oxidising and reducing agents. Para-quinonoid compounds give reduction products which are difficult to re-oxidise, whereas those of ortho-quinonoid bodies are

[1] Green and Woodhead, *J.C.S.*, 1910, xcvii, 2388; 1912, ci, 1117. Green and Wolff, *Ber.*, 1911, xliv, 2570; *J.S.D.C.*, April 1913. Green and Johnson, *J.S.D.C.*, Dec. 1913.

easily re-oxidised. As Aniline black behaves in the latter manner it is considered to possess an azine structure, and, from evidence yielded by much experimental and analytical work, Green has finally concluded that it is a salt of triphenyl azonium-octaphenazine.

The oxidation of aniline may be directed, at will, to produce either the indamine or the azine structure. When conducted throughout in strong acid solution the indamines are obtained by direct quinonoid addition; emeraldine, nigraniline, and pernigraniline being formed successively. Further oxidation under the same conditions yields quinone—never Aniline black, which is formed only in neutral or weak acid solution as already mentioned. If, however, the acid oxidation mixture has been so balanced that, at the nigraniline stage, the solution has become approximately neutral, further oxidation then yields the azine compound—Aniline black—provided sufficient free aniline remains. An insufficiency of acid at the beginning of the oxidation promotes the formation of undesirable by-products at the expense of nigraniline—brown insoluble bodies and soluble violet colouring matters which weaken and spoil the shade of the ultimate black. The mechanism of the reaction is altered, the quinonoid addition taking place indirectly instead of directly, as required for nigraniline.

The difficulty, therefore, of producing an ungreenable Aniline black in a single phase, is that the initial stages of the oxidation demand strongly acid conditions in order to yield the necessary amount of nigraniline, and to avoid detrimental by-products, whereas, on the contrary, the final stages require, more or less, neutral conditions to bring about the azine structure of ungreenable black. Moreover, it is essential to retain in the black mixture a certain amount of free aniline until the final reaction is completed; otherwise the black is not ungreenable.

In older processes, as already described, these difficulties are met by dividing the oxidation into two separate and distinct operations; the first (ageing) having for its object the production of emeraldine or nigraniline, and the second (usually a chroming process) the conversion of these bodies into ungreenable Aniline black. During the steam-ageing great care must be taken to avoid driving off the free aniline, since, in its absence, the only effect of the subsequent chroming will be to convert the nigraniline into pernigraniline—an unstable compound of an unpleasant purple shade of black. In plain shades the free aniline may be added to the chrome bath, but this is obviously impossible in the case of printed goods, as it would stain the white parts of the fabric; hence the necessity for carrying forward sufficient free aniline to the second stage of the oxidation.

One of the most troublesome features of the majority of Aniline blacks in current use is their tendency to injure the fabric owing to the liberation of a large amount of hydrochloric acid, which, in the absence of anything to absorb it, attacks the fibre with the formation of hydrocellulose.

In the case of Prussiate blacks the liberated acid is more or less neutralised by the potassium ferrocyanide, and the danger is consequently less pronounced; but in all other mixtures depending on aniline salt (the hydrochloride) for their essential aniline content, the free acid constitutes an inherent defect which cannot be overcome to any practicable extent by the addition of an excess of aniline to the printing colour, although this addition, certainly, is useful in preventing the tendering of the fabric during printing and subsequent drying, and in protecting the doctors from corrosion. The evolution of hydrochloric acid gas, during ageing, from these types of Aniline blacks is readily explained, in the light of present knowledge, by the difference which exists between the number of molecular proportions of acid contained by a given weight of aniline salt, and the number, capable of being absorbed by the

corresponding quantities of nigraniline (and Aniline black), resulting from its oxidation. Thus, the eight molecules of aniline-salt required for the preparation of *one* molecule of nigraniline contain eight molecules of hydrochloric acid, of which two only are absorbed by the nigraniline, the rest being split off in the free state. Apart from its own particular form of destructive action on the cotton fibre, this free acid is, further, distinctly favourable to the liberation of oxides of chlorine, which, under the conditions usually obtaining in ordinary agers, are extremely liable to attack the fibre, converting it into oxycellulose, and, consequently, tendering it.

Had Aniline black been a less important colour the difficulties and dangers attendant on its application in calico printing would long since have caused it to fall into disuse; but its value, both as regards beauty of shade and exceptional fastness to light and soaping, has been so universally recognised that, on the contrary, its use has extended enormously, and its perfection has been, perhaps, the subject of more investigation than that of any other single colouring matter. When it is remembered that the constitution of Aniline black was unknown for fifty years after its first introduction, it is astonishing to note how the keen observation and constant experiment of the earlier investigators enabled them to establish processes which, in principle, accord so closely with modern theory. Many of these processes are excellent up to a certain point, and quite suitable for most purposes, but for the fastest work they leave much to be desired. By none of them can an ungreenable, non-tendering black be obtained with *certainty,* though at times such a result is achieved.

In recent processes, however, the various defects incidental to the printing of Aniline black have been more or less overcome; and if the formulæ suggested to this end are not as yet quite perfect in all respects, they at least permit of a single-phase ungreenable black being obtained without any tendering of the fibre.

The different methods suggested for the realisation of such single-phase ungreenable blacks fall into two main groups, viz. (1) those depending on the use of relatively feeble acids only; and (2) those in which the employment of two or more energetic catalysts is combined with a nice adjustment of mineral and organic acids in such manner that the oxidation proceeds smoothly and rapidly, the liberated acids, and oxides of chlorine, being taken up by the aniline as soon as they are evolved and before they can attack the fibre.

In the first group, the most interesting example is the method of A. Scheurer (*Pli cacheté* No. 1414, 1903), published by the Société Industrielle de Mulhouse (November 1919). In this process the only characteristic feature is the employment of the rather unusual hydrofluosilicic acid, which is found to be sufficiently strong to promote the formation of emeraldine, and, at the same time, not too acid to prevent the ultimate oxidation to the ungreenable black stage.

The formula given is as follows:—

35	grms.	red prussiate of potash.
35	,,	chlorate of soda.
65	,,	aniline oil.
105	,,	hydrofluosilicic acid 33° Tw.
760	,,	starch paste $12\frac{1}{2}$ per cent.
1000		

This colour keeps well, and presents the peculiarity of containing neither copper nor vanadium salts nor any hydrochloric acid apart from the small

quantity generated by the reduction of the chlorate. It possesses the further advantage of having no action on the doctor. Its development is effected either by ageing in the rapid steam ager or by hanging for forty-eight hours in a damp atmosphere at a temperature of 45° C. In the latter case the oxidation takes place in two stages; during the first twenty-four hours emeraldine is formed; twenty-four hours later the emeraldine is oxidised and completely transformed into ungreenable Aniline black, quite unaffected by sulphurous acid. Other blacks of this simple type in which acetic, formic, or lactic acids are employed are not successful, and call for no special mention.

In the second group the outstanding feature is the use made of special bases such as paraphenylenediamine, meta-toluidine, para-aminophenol, etc., which when mixed with aniline in small proportions play the rôle of very active catalysts. In larger proportion they act also as veritable colouring matters, the brown shades they yield on oxidation effectually masking any greening of the aniline component. In this connection, however, they are of limited application only as they impart a brownish tone to the black, which is not suitable for most purposes; hence their chief use is as catalysts pure and simple; the ungreenableness of the ultimate black depending on the proper oxidation of the aniline. Paraphenylenediamine is the most important of these organic catalysts.

The introduction of paraphenylenediamine in connection with Aniline blacks was first suggested by P. Monnet in 1886, with the object of obtaining, in dyeing, a black capable of resisting the greening action of sulphur dioxide. Monnet observed that an addition of 0·5–1·0 per cent. of paraphenylenediamine and similar bases to ordinary aniline blacks had the remarkable effect of rendering them quite ungreenable (German pat. 4257, May 11th, 1886). In all probability this result is brought about by a reaction analogous to that which takes place during the formation of Aniline black by Green's process, but such was not noted by Monnet, whose colours contained the usual ingredients of the oxidation blacks of his time

For some unknown reason Monnet's process never became general, and was practically forgotten until the introduction of Paramine brown, in 1905, recalled it to the attention of colourists. Previous to this many attempts had been made to prevent the formation of hydrocellulose by substituting for a portion of the hydrochloric acid various weaker acids and acid salts (phosphoric, arsenic, and boric acids—Beltzer; lactic acid and its salts—Boehringer; formate of alumina—Eberle), but none of these methods was entirely successful, for while they certainly reduced, to some extent, the liability to tendering, they yielded, in practice, but indifferent blacks. Even when combined with paradiamines the results were little better.

The publication of Green's work (1907) on the effect of paraphenylenediamine on the oxidation of aniline in weak acid solution re-awakened interest in the production of one-phase ungreenable Aniline blacks, and many inventions relating to the subject have been patented in recent years. None of these inventions appears to involve any new principle, their originality consisting for the most part of ingenious combinations of the essential conditions established by previous workers in the same field; such differences as they do exhibit are to be found mainly in refinement of process, and balance of parts in accordance with modern conceptions on the constitution and mode of formation of Aniline black. Certain aspects of the problem of obtaining an ungreenable black, of good printing quality, on unprepared cotton cloth, still await solution; but that a large measure of success has been achieved in this direction is sufficiently demonstrated by the results obtained by E. A. Fourneaux, whose processes form the subject-matter of a series of patents

granted to him and the Calico Printers' Association, Ltd., between 1908 and 1918. The general direction of the lines of attack on the problem are perhaps most clearly indicated by the following résumé, based on information furnished in a private communication from the inventor:—

The object in view was to produce an ungreenable black which might be applied without the exercise of special precautions, capable of being developed by steam ageing with the least possible danger of tendering the fibre, and substantially free from intermediate products on its emergence from the ager.

For this purpose it was proposed to use only as much hydrochloric acid as the black base, formed in ageing, is capable of absorbing (between $2\frac{1}{2}$ and 3 molecular proportions to 11 molecular proportions of aniline), an amount of a relatively strong volatile acid, such as formic acid, sufficient to prevent indirect quinonoid addition, and powerful catalysts, organic and inorganic, in combination with alkali chlorates.

Curiously enough such mixtures do not necessarily tender the fibre less than similar mixtures containing the normal proportion of hydrochloric acid, but, unlike the latter, the new mixtures tender the less the more rapidly and smoothly the formation of black takes place—a fact which led to the important conclusion that under conditions favouring a rapid and smooth formation of black the oxides of chlorine, generated from the chlorate by the action of the catalysts, affect the aniline, by selective action, in preference to the fibre, while under opposite conditions oxycellulose may be formed to such an extent as to counterbalance any advantage gained by preventing the formation of hydrocellulose.

Even after the best relative proportions of the ingredients had been established by experiment, the results were found to be irregular in practice,—a defect caused by losses of aniline in drying and ageing. This difficulty was met by the addition of comparatively weak mineral acids, such as boracic and meta-phosphoric acids, which were found to prevent the evaporation of aniline from aqueous solutions far more effectually than even the non-volatile organic acids, and that without materially inhibiting the formation of ungreenable black.

On adapting the process to air-ageing it was found that while oxidation proceeded readily to the diphenylazonium stage, complete oxidation was so slow and difficult that it was preferable to stop at the intermediate stage and complete the reaction by a light chroming.

The foregoing principles have been applied, by the inventor, to Prussiate blacks by neutralising a portion of the excess acid with alkali metaphosphate or metaborate, but in this case the black, though greatly improved, is not ungreenable.

It is well known that on ageing all Aniline blacks give off noxious vapours consisting of acids, oxides of chlorine, and aniline. The acid vapours tend to prevent the formation of ungreenable black, the oxides of chlorine to over-oxidise and destroy the intermediates, and all three combined to produce a pink colouration (similar in composition to magenta) on the white parts of the cloth. The colouration frequently takes the form of a pink or violet halo round the printed pattern; at other times it is general or in patches, these latter being caused by traces of acid left in the cloth after bleaching. If the pinkish stains are general, or occur as halos, they indicate that the ageing conditions are unfavourable, their appearance being due to the formation of magenta-like compounds resulting from the oxidation of aniline vapours by oxides of chlorine in presence of acid vapours. On most ageing machines the only ventilating arrangement provided is an opening at the top, so that whatever ventilation takes place is in the nature of an overflow, and therefore

inefficient. Nor is a forced draught much better, as a right-angled bend in the outlet pipe or a heavy wind may render it quite ineffective.

A patent recently granted to the Calico Printers' Association, Turner and Fourneaux, overcomes the difficulty by means of suction elements inserted between the folds of the fabric and connected with an efficient ejector-condenser. In this manner the vapours are removed as soon as generated, the ventilation can be perfectly regulated, the tendency to the formation of pink stains is reduced to a minimum, and, with a suitable formula, the production of an ungreenable black is ensured. For blacks of the type just described the best results are obtained by regulating the ventilation so as not to remove the whole of the vapours and by introducing the steam under pressure in such volume as to maintain approximately atmospheric pressure within the ager. The temperature is best kept at about 205° F., and the steam rendered moist by allowing it to impinge on water in the bottom of the ager.

From the foregoing it will be seen that the basic principles involved in the production of ungreenable blacks may be summarised under the following heads:—

1. The proportion of mineral acid is reduced to that which the black formed is capable of absorbing. This prevents tendering due to hydrocellulose.

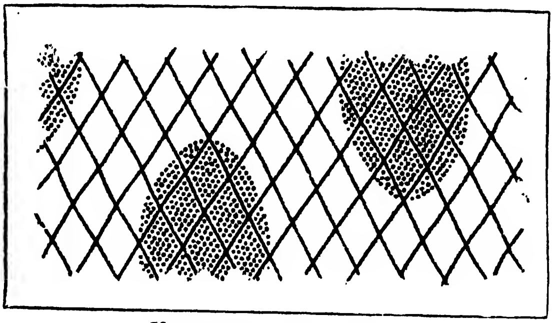
2. The formation of brown by-products is avoided by the addition of another acid, which must be strong but not capable of forming hydrocellulose under working conditions.

3. The free aniline is carried partly by the thickening and partly by means of phosphoric acid, boracic acid, or their equivalents.

4. The formation of oxycellulose is prevented by the use of energetic catalysts and by adjusting the proportion of the constituents in such manner that the oxidation takes place rapidly and completely, the theory being that the oxidising gases are absorbed by the aniline as quickly as they are generated.

5. Rapid oxidation is essential, and is greatly facilitated by a special type of ager (patented).

The improved oxidation blacks are produced in a single ageing operation, and require no subsequent chroming; they may also be resisted by means of alkali sulphites and the like. Further, they are adapted either for printing or for slop-padding, and, in most cases, they may be employed for exactly the same purposes as the blacks in general use.



Ungreenable Aniline Black.
Fourneaux's process.

The following formulæ [1] will illustrate the practical application of the above principles:—

[1] Eng. Patent, 116562 (1917).

UNGREENABLE BLACK (printing).[1]

75	grms.	starch.
300	,,	gum tragacanth mucilage.
32	,,	aniline.
44	,,	aniline salt.
4·5	,,	paraphenylenediamine di-hydrochloride.
40	,,	formic acid 90 per cent.
34	,,	boracic acid.
41	,,	chlorate of soda.
40	,,	copper sulphide, 24 per cent.

To 1000 grms. with water.

Print, age, wash, and soap. No chroming is necessary, but it is not detrimental, and may sometimes be required if the ageing has not been carried out properly.

For plain blacks, produced by slop-padding, it is possible to reduce still further the mineral acid content of the mixture.

Thus :—

SLOP-PAD UNGREENABLE BLACK.

35	grms.	starch.
150	,,	gum tragacanth mucilage.
54·5	,,	aniline.
27·75	,,	aniline salt.
3·25	,,	paraphenylenediamine di-hydrochloride.
90	,,	formic acid 90 per cent.
48	,,	lactic acid 30 per cent.
40	,,	boracic acid.
52	,,	chlorate of soda.
8·25	,,	copper chloride.

To 1000 with water.

Slop-pad, dry carefully, and proceed as for the printed black.

Aniline blacks at all times are difficult colours to print satisfactorily, and, in common with the rest of its class, the above printing black requires special care at every stage of its production. So far as ageing is concerned, it is most important to ensure a thorough ventilation of the ager, otherwise oxidation is retarded and tendering promoted by the accumulation of acid vapours. The best results with the above blacks, and indeed with all Aniline blacks, are obtained by ageing them in an ageing machine fitted with the special suction elements patented by the Calico Printers' Association, Turner and Fourneaux.[2] These elements are introduced between the laps of the cloth and carry off the vapours as they are evolved, thus maintaining an atmosphere of relatively pure steam.

One very valuable property of all Aniline blacks is that previous to oxidation they are very susceptible to the action of alkalies and neutralising and reducing agents. The presence of any one of these three classes of bodies is sufficient to prevent entirely the development of the black; so that, on washing the goods after ageing, the cloth remains perfectly white in those places where such reagents have been applied. The practical application of this property to the production of white and coloured designs on a black ground constitutes an important special style, which will be dealt with under the heading of "Resists and Discharges."

[1] Eng. Patent, 116562 (1917).
[2] Eng. Patent, 136507 (1919).

THE VAT COLOURS.

By a *vat colour* is understood an organic pigment which, though insoluble in all solvents usually employed in printing and dyeing, is capable of yielding a soluble leuco compound when treated with alkaline reducing agents, and, in this form, of being absorbed by the textile fibres in which it is subsequently re-oxidised to its original colour and state of insolubility, thus producing a fast dye.

Indigo, the best known and perhaps even yet the most important of all colouring matters, is a typical vat dye, and was, for a long time, almost the only representative of the valuable series of which it now constitutes merely the first member. The successful introduction into commerce of synthetic Indigo, in 1897, however, led almost immediately to a notable increase in the number of vat colours. Derivatives of Indigo (and its isomer Indirubin) appeared in quick succession, and, concurrently, it was discovered that certain derivatives of anthraquinone, and later of carbazol, could also be applied as vat colours. During the last twenty years upwards of a hundred new members of the group have been placed on the market; and, as might be expected from the considerable differences they exhibit in chemical structure, they give a striking variety of shades and demand a certain amount of individual treatment in practice, though, as mentioned above, they are all applied according to the same general principles.

The chemistry of the vat colours is far too complex a subject to deal with adequately in these pages, and all discussion of it therefore will be omitted, except on such points as have a practical bearing on the application of the colours themselves. Full information on the subject is easily accessible in such works as *The Synthetic Dyestuffs*, by Cain and Thorpe, and other works dealing more or less exhaustively with the various aspects of the modern dyestuffs industry.[1]

A consideration of the constitution of the numerous members of the vat-colour group, however, shows that, broadly speaking, they fall into three distinct sub-groups, viz. :—

1. Indigoid vat colours.
2. Anthraquinone vat colours.
3. Sulphurised vat colours.

A few colours possess properties intermediate between those of two groups, but with these exceptions the groups are fairly sharply defined.

1. *The Indigoid Vat Colours.*—Under this heading are included Indigo and its halogen and sulphur derivatives, the Ciba series, the Helindone series, the Thioindigo series, and the Durindone series. Except in the case of Indigo, these colours are generally reduced by means of sodium hydrosulphite; and, as their leuco compounds are readily soluble in weak alkalies, they are suitable for dyeing and printing both vegetable and animal fibres. Indigo itself may be reduced in many ways, according to the purpose for which it is required. In *plain dyeing* it is immaterial whether sodium hydrosulphite, zinc dust, ferrous sulphate, etc., are used, and the alkaline component of the vat may also vary between soda, potash, and lime. In Indigo *printing*, however, the reducing agents are confined to either sodium hydrosulphite or glucose, and the full development of the colour can only be obtained in presence of concentrated solutions of caustic alkalies (caustic soda as a rule). From this

[1] *Synthetic Dyestuffs, etc.*, Cain and Thorpe. (C. Griffin & Co., Ltd.)
A Manual of Dyeing, Knecht and others. ,,
The Analysis of Dyestuffs, A. G. Green. ,,

it is obvious that Indigo is quite unsuited to the printing of any but the vegetable fibres, though in dyeing it is applicable to both animal and vegetable fibres. The Indigoid dyestuffs are characterised by their solubility in boiling benzene, glacial acetic acid and formic acid, and especially in boiling pyridine, which readily strips them from the fibres. Some of these solutions are fluorescent and all are highly coloured. The colours are also volatile when heated strongly, but do not form particularly distinctive vapours, except in the case of Indigo and its halogen derivatives, which evolve violet fumes.

When reduced with hydrosulphite of soda and caustic soda, all Indigoid dyestuffs give light yellow vats (solutions of the leuco compound), from which the original colour is regenerated, and precipitated, on re-oxidation by exposure to the air, or otherwise.

2. *The Anthraquinone Vat Colours.*—This group includes the Indanthrene, Cibanone, Alizanthrene, Algole, and Caledon series, and also Helindone Blue 3 G. and Helindone Yellow 3 G.N.[1] With these are also classed the sulphur derivatives of anthracene and anthraquinone (known under the names of Cibanone orange, yellow, brown, and black), and the Alizarin Indigo group, which may be regarded as intermediate between the Indigoid and Anthraquinone groups, possessing properties common to both. With very few exceptions the anthraquinone colours are insoluble, or very sparingly soluble, in boiling pyridine, benzene, and glacial acetic and formic acids; neither are they volatile on heating—two characteristics which serve to distinguish them from the colours of the Indigoid group. A further distinction is to be found in their behaviour towards alkaline reducing reagents, which convert them into *highly* coloured leuco compounds—red, blue, orange, and purple—very much darker in shade than the original colours, and usually of a totally different colour to the final dyed effect.

In dyeing with anthraquinone colours, the reducing agent employed is almost always hydrosulphite; in printing, the choice is wider—stannous hydrate, glucose, hydrosulphite, and mixtures of these being used for steam styles and ferrous sulphate in combination with stannous chloride for styles developed by an after-treatment in caustic soda.

3. *The Sulphurised Vat Colours.*—Although in a general way this description would apply to all sulphur-containing vat dyestuffs, it refers in a particular sense to only such of them as do not appear in the two preceding categories.

Up to the present the group is only represented by a few members, viz.: the Hydron blues, Hydron violet, and the Carbindole blues. These colours do not sublime on heating and are insoluble in boiling pyridine, in which respects, and also in their mode of formation—by the action of polysulphides or sulphur on certain organic bodies—they bear a close relation to some Cibanone colours on the one hand and the ordinary sulphide colours on the other. From the former they are distinguished by being derived from carbazol instead of anthraquinone and anthracene, and from the latter by their insolubility in sodium sulphide. They yield light yellow leuco compounds on reduction, which re-oxidise rapidly, and their general method of application is identical with that of other vat colours. They are used exclusively for the printing and dyeing of vegetable fibres, upon which they give full dark shades of great fastness to light and soaping. The blues resemble Indigo very closely and are much more permanent. The "Hydron" group does not consist entirely

[1] Chloranthrene and Duranthrene colours have been renamed and are now included in the Caledon series. Similar changes have occurred in the case of many Helindone, Thioindigo and Algole colours, these being now called Indanthrene or Algole, according to fastness.

of colours of the above class. Hydron Yellow G. is not a sulphur vat colour, and Hydron olive and brown are probably identical with, or similar to, the corresponding Indanthrene and Cibanone colours.

Generalities.—The vat colours, as a class, are distinguished above all others for their remarkable fastness to acids, alkalies, soaping, light, bleaching, and other destructive agencies—in fact no other colour approaches them in all-round permanence unless it be genuine Turkey red. Moreover, an enormous range of shades can be obtained by their means, and they lend themselves to a great variety of styles. They can be dyed, padded, printed, reserved, and discharged under proper conditions, and also used for the production of coloured discharge effects on dyed grounds of other classes of dyestuffs, and even, in some instances, on grounds of vat colours themselves. Of course individual members, here and there, fall short of the general high standard of fastness in certain particulars, but, with these few exceptions, the vat colours are practically as permanent as the cloth upon which they are dyed or printed; and even the failure of the few exceptions is of little moment, as they can easily be replaced by other members of similar shade.

Owing to their insolubility the vat colours require to be ground very finely before any attempt is made to reduce them; for this reason they are usually sent out in paste form.

The expense of vat colours confines their use to the highest class of work—shirtings, casement cloths, and some dress and furniture prints—in which fastness to light, soaping, and laundering is of the greatest importance.

Until the beginning of the war, in 1914, the manufacture of vat colours was a close monopoly of the German and Swiss colour firms. During the last few years, however, British chemists have succeeded in overcoming the technical difficulties of many of the processes, and it is gratifying to record that, although there are yet gaps in the series, a considerable number of very valuable colours of our own manufacture is now available for use. These appear on the market under the following names:—Indigo L.L.; Caledon colours (I.C.I.); Durindone, and Carbindole colours (I.C.I.); and Hydranthrene colours (L.B.H.).

Indigo Printing.

Indigo is a natural colouring matter obtained by a special treatment of the leaves of various species of *Indigofera*, which are largely cultivated in India and the East Indies generally. Like the essential colouring principle of Madder—Alizarin—Indigo is now manufactured artificially. Synthetic Indigo comes into the market as a 100 per cent. powder or a 20 per cent. paste, and its purity, regularity of composition, fine state of division, and the ease with which it can be applied without a prolonged grinding, are such that it has now replaced the natural product in calico printing, and to a great extent also in dyeing. It possesses exactly the same properties as the natural dyestuff, and is applied by exactly the same methods. Its chief recommendation to the calico printer is that it is remarkably free from gritty and sandy substances, and that, in dyeing, it can be used at once without any preliminary grinding, and, in printing, it only requires grinding for a short time—often not at all—and can be strained very easily. On the other hand, natural Indigo always contains hard, sandy particles, which are most difficult to remove, even by the most careful straining through fine cloths; and as it comes into commerce in the form of hard, dry cakes, or cubes of variable composition, it always

requires to be analysed before it can be used, and then ground for a week or so before it is fit to be employed for printing.

One of the greatest difficulties encountered in printing natural Indigo is due to the presence of gritty matter, which plays havoc with engraved rollers, and it is largely owing to its absence in the synthetic product that the latter has had so favourable a reception.

Artificial Indigo, however, has the defect of its quality. It is not quite so fast to washing as the natural dyestuff, and this has been put down by some chemists to its purity—that is, to its being pure indigotine, unmixed with indirubin, indigo-brown, and other organic bodies, which are asserted to exercise a beneficial effect on the fastness of natural Indigo. Be that as it may, the difference between the fastness of natural and artificial Indigo is too slight to cavil about, and certainly has had no effect in checking the employment of the latter.

The methods of applying Indigo to the cotton fibre, either by dyeing or printing, are all based on its property of being converted by reducing agents into a body known as "indigo-white" which is soluble in alkalies, and, in that form, capable of penetrating into the body of the fabric to which it has been applied, and of being re-oxidised therein to a permanent blue dye. The methods of dyeing and printing vary in detail rather than principle. In the former case the cloth is merely steeped in an alkaline solution of indigo-white and then exposed to the air in the wet state. The yellow-coloured solution absorbed from the dye vat becomes first green and then gradually bluer and bluer, until finally the whole of the indigo-white is re-oxidised to insoluble blue Indigo, and the cloth is found on washing to be permanently dyed. In printing, the reduction of the Indigo, its solution in alkali, and its subsequent re-oxidation all take place on the cloth itself.

Earlier processes of printing Indigo, being based upon the method adopted in dyeing, depended upon the direct application, to the fibre, of thickened solutions of indigo-white as such. These processes were very difficult to control—the rapid oxidation of the indigo-white rendering it almost impossible to obtain regularity of shade—and, although certain of them were, to some extent, employed in practice, they were never satisfactory, and they one and all became obsolete immediately upon the publication, in 1883, of Adolf Schlieper's glucose process.

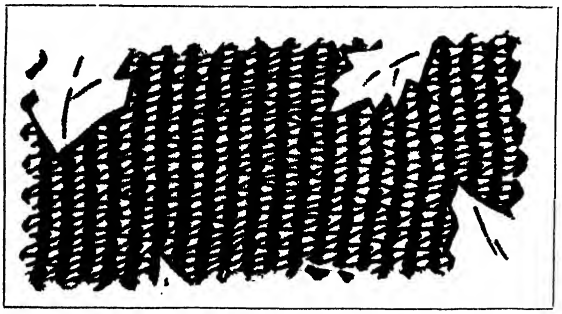
In 1922, however, the idea of printing indigo-white was resuscitated by Messrs Durand and Huguenin, of Bâle, who solved the problem by the introduction of Indigosol O., a soluble and stable compound of indigo-white—so stable indeed that it requires fairly energetic oxidation to re-convert it into Indigo. This product is applicable to a wider range of effects than is Indigo itself but, so far, its price has proved a bar to its general use for standard Indigo styles.

Methods of producing Indigo on the fibre from indoxyl, *o*-nitrophenylpropiolic acid, formaldehyde-indigo white, etc., are no longer in use, and are mentioned here solely for the sake of their historical and scientific interest.

"Indigo Salt T" (Kalle), *o*-nitrophenyl-lacto-ketone, still finds a limited but ever-decreasing application for the printing of special styles ; its bisulphite compound yields Indigo on treatment with caustic soda.

Practically speaking there are only two methods of printing Indigo with any degree of success: (1) the Glucose or Schlieper and Baum process ; (2) the hydrosulphite process. They are both in common use, and there is nothing to choose between the results obtained: they are equally good. The glucose process is the older and cheaper of the two, and will be taken first.

The Glucose Process.—This elegant process was perfected at the works of Messrs Schlieper, Baum & Co., and was for a long time the only method of completely utilising the Indigo employed. It depends upon the powerful reducing action of grape sugar in alkaline solutions; and as the reaction takes place either in the cold or at a slightly elevated temperature, it is essential that the grape sugar or glucose and the alkali should not be mixed together before the Indigo is printed, as otherwise reduction and partial reoxidation of the latter would occur in the colour tub instead of on the cloth. To avoid this, which would result in unevenness, the cloth is first prepared in a 10–25 per cent. solution of glucose, then dried and printed with a mixture of Indigo and caustic soda.



Indigo (Glucose Process).

The preparation of the white cloth is effected in a padding mangle through the following solution:—

Glucose Prepare 25 per cent.

250	grms.	grape sugar.
750	,,	water.
1000		

Dry the goods thoroughly (but not too hard), and then print them in the colour below.

Dark Indigo Blue 3 per cent.

150	grms.	Indigo L.L. 20 per cent. paste (I.C.I.).
850	,,	alkaline thickening.
1000		

Alkaline Thickening:—

30	grms.	maize starch.
100	,,	dark British gum.
870	,,	caustic soda 77° Tw.
1000		

Mix carefully; heat to 140° F., and cool before use.

A 20 per cent. Indigo paste may also be made by grinding together 200 grms. of Indigo L.L. in powder and 800 grms. of 4 per cent. gum Senegal solution. If the printing colour is too thick, it may be thinned by replacing part of the thickening by caustic soda 77° Tw. thus:—

Indigo Blue (thin).

150	grms.	20 per cent. Indigo L.L. paste.
700	,,	alkaline thickening.
150	,,	caustic soda 77° Tw.
1000		

For lighter shades of Indigo it is only necessary to reduce the quantity of Indigo paste, making up the kilogramme with caustic soda at 30° Tw.; or the following reducing paste may be used:—

REDUCING PASTE.

600	grms.	alkaline thickening.
385	,,	40 per cent. gum Senegal solution.
15	,,	glycerine.
1000		

	Medium.	*Light.*	*Pale.*
Dark Indigo blue, 3 per cent.	1 part	1 part	1 part
Reducing paste	3 parts	5 parts	10 parts or more.

If light shades only are printed, the strength of the glucose preparation may be reduced to as low as 10 per cent., but it is not advisable to go below this point lest the colour should suffer.

Steaming.—The reduction of the printed Indigo is brought about by a short passage through air-free moist steam at a temperature of not lower than 100° C., and it ought to be proceeded with as soon as possible after printing. If the goods are allowed to lie exposed to the air the caustic soda absorbs carbonic acid, and its power of reacting with the glucose and Indigo diminishes in proportion as it becomes carbonated.

The actual conditions under which glucose-Indigo prints are steamed vary considerably in different works, and, from the fact that good results are claimed for each method, it would appear that no one set of conditions can be laid down as the best.

That steam at about 100° C. is an essential factor to success is generally acknowledged; but the degree of its humidity, the duration of its action, and the advantage of using it at a still higher temperature are questions upon which a great diversity of opinion exists. In some works the printed goods are steamed in an ordinary rapid ager working at 100° C., and provided with means for ensuring the presence of moisture and the absence of air. A passage of ½–1 minute is, as a rule, sufficient to effect the complete reduction of Indigo to indigo-white. Better and more regular results are, however, obtained in the special Indigo ager already described (see fig. 62), in which steam enters the chamber through boiling water, and thus becomes thoroughly saturated with moisture, with the result that all the conditions essential to the perfect reduction of the Indigo, and to its solution in the caustic soda of the thickening, are obtained, namely, humidity, a high temperature, and the absence of air. In the ordinary rapid ager these conditions are not easy to maintain; and although, with care and constant attention, it is possible to obtain satisfactory results in this type of ager, the colour is more often than not reduced irregularly, and, on re-oxidising, is found to be uneven. The presence of air prevents the complete conversion of the Indigo into indigo-white and, if the steam is at all deficient in moisture, the solution of the indigo-white is partial only, and its penetration into the fibres of the cloth more or less irregular. A good deal of colour remains on the surface, and is washed off in the subsequent processes; so that not only is the work spoilt, but a considerable amount of a valuable colouring matter is lost, not to speak of the labour and delay that may be involved in the production of spoilt work. Equally satisfactory, and perhaps even more regular and consistent, results are obtained by steaming in the high-temperature hydrosulphite ager (see fig. 61) at 102°–104° C. dry-bulb and 100°–102° C. wet-bulb thermometers. The passage may occupy from 1½–4 minutes, but ought not to be prolonged beyond the time necessary for the

proper reduction of the Indigo ; too long a steaming is apt to impair both the depth and the purity of the shade.

Opinions as to the beneficial influence of moisture are contradictory, some printers asserting that they have achieved success with *dry* steam alone, while the majority maintain that damp, and even saturated, steam is absolutely essential to the fullest utilisation of the Indigo. The experience of all printers, with a reputation for Indigo work, points emphatically to the advantage of using *moist* steam, and, as their practice is based upon a long series of observations and bulk experiments, their dicta may be accepted as final.

Whatever method of steaming may have been adopted, the colour of the Indigo, as the goods emerge from the ager, ought to be a *brownish olive* ; if it is *yellow*, the reduction has been pushed too far, and the colour will never re-oxidise fully ; if it is *green*, the reduction is incomplete, and only a portion of the Indigo will be fixed, the rest washing off in the subsequent operations of souring, washing, and soaping.

Re-oxidation.—Formerly, after ageing or steaming, the printed pieces were suspended on rails in a cool hanging room, through which fresh air was allowed to circulate freely between each fold of the hanging cloth, and the floor of which was covered with damp sawdust or peat. In this chamber the pieces remained until the indigo-white was re-oxidised to Indigo, which is insoluble and becomes permanently fixed on the fibre. The last traces of indigo-white were converted back into Indigo by washing the goods in a copious supply of fresh running water, and this was followed by a treatment in dilute sulphuric acid (1°–2° Tw.), and a second thorough wash in water. Modern practice has discarded the hanging rooms in favour of a short passage through solutions of oxidising agents, such, for example, as the two following:—

CHROME BATH :—	I.	II.
Bichromate of soda . . .	7·5–10 grms.	20 grms.
Sulphate of ammonia . .	..	10 ,,
Water	1000 ,,	1000 ,,

As the bath becomes alkaline and exhausted replenish with :—

6	grms.	sulphuric acid 168° Tw.
20	,,	bichromate of soda.
1000	,,	water.

Both solutions are used cold ; No. I. for general Indigo prints such as shirtings, light blotches, pads, resists under covers, etc. ; No. II. for direct prints only in dark shades and heavy patterns.

Light shades of Indigo can be re-oxidised readily and completely by washing in running water immediately after steaming, and without the necessity of any intermediate hanging or chroming as above. The goods should be cooled first, and the wash waters should also be as cold as possible, otherwise the large quantity of alkali present is liable to be dissolved out of the cloth too rapidly, and thus cause the indigo-white in solution to "run" before it is oxidised.

Whether the Indigo has been re-oxidised by exposure to the air or by chroming, the goods are finally well washed and soaped if necessary. The operations of souring and washing (in the case of air oxidation) and of chroming are conducted in the open width in order to prevent the Indigo from marking off before it is properly fixed. The final soaping and washing may, however, be performed in rope state, as the colour is by then fully developed and fixed.

The well-known "red and blue style" can be produced perfectly by the glucose process of Indigo printing. Turkey-red dyed cloth is prepared in a

solution of glucose, printed with Indigo blue 3 per cent., then aged, hung, washed, and soaped as above. The Alizarin-alumina lake of the Turkey red is dissolved out (or discharged) by the caustic soda of the Indigo printing colour, and thus leaves a comparatively white foundation under the blue. The unprinted parts of the cloth remain unaffected by the alkali; so that, according as a blotch or an object is printed, a red design on a blue ground or a blue design on a red ground is obtained.

By printing other strongly alkaline colours—*e.g.* plumbite of soda—along with the Indigo or mixed with it, it is possible to produce coloured patterns in white, blue, green, or yellow on a red ground. After ageing, such goods are passed through a bath of silicate of soda, then well washed and treated in an acid solution of bichromate of potash, which precipitates the lead as Chrome yellow. Green is obtained from the mixture of Indigo and plumbite of soda, and white from a thickened solution of caustic soda containing tin and zinc, etc. This style of work will be described in detail in its proper place under "The Discharge Style."

By combining glucose with the naphthol prepares used for the development of the Azoic colours, on the fibre, it is possible to print Indigo, by the glucose process, in conjunction with Paranitraniline red and similar colours. The naphthol part of the prepare must not contain more soda than is required for keeping the β-naphthol in solution, otherwise the glucose will be decomposed to an extent which will render the proper reduction of the Indigo impossible. The following is an example of a prepare formerly used in practice:—

GLUCOSE-NAPHTHOL PREPARE.

a	25	grms.	β-naphthol.
	50	,,	caustic soda 36° Tw.
	200	,,	water.
b	300	,,	glucose (chips).
	395	,,	water.

Dissolve *a* and *b* separately, and when they are quite cold mix them together and make the whole up to one litre with cold water. Pad the cloth in this solution, and dry in warm air at as low a temperature as is convenient; print on Indigo blue 3 per cent. and any suitable diazo-compound, such as that of paranitraniline or α-naphthylamine; age as usual to reduce the Indigo, and then, after allowing the goods to remain exposed to the air for a few hours, wash them in a plentiful supply of fresh running water. Finally, soap them in the rope form and dry.

This process was formerly used for the printing of two- and three-colour patterns, *e.g.* Indigo blue, Paranitraniline red, and α-Naphthylamine claret, but since the introduction of the hydrosulphite process of Indigo printing, which dispenses with the glucose preparation, it has fallen into disuse. A certain amount of the glucose was always wasted, and the prepared cloth, in any case, had to be dried and treated with extra care before printing.

The glucose process, though still largely used for the printing of pure Indigo styles, has been replaced, in a great measure, by the more convenient and rapid hydrosulphite process, which is adaptable to all styles of Indigo work, and to a wide range of mixed effects in addition.

The Hydrosulphite Indigo Process.—The distinguishing feature of the hydrosulphite process of Indigo printing is the simultaneous application of the colouring matter, its reducing agent, and its alkaline solvent. The printing colours are very stable, as the reducing agent (hydrosulphite-formaldehyde)

has no action on Indigo in the cold. The hydrosulphite process is not cheaper than the glucose process—in fact the printing colour itself is dearer—but it has the advantage that no preparation of the cloth is required before printing, and therefore the rate of production is increased, and some economy effected in labour, time, and steam by dispensing with the use of the padding and drying machines. Moreover, as all the essential elements of the colour are mixed together in a stable paste, which only decomposes when subjected to a high temperature, the goods can be printed at any time without the necessity for making special arrangements. Neither is the hydrosulphite process so dependent for success upon certain conditions of moisture and duration of steaming as is the glucose process. In fact, so long as the temperature of the steam is sufficiently high to bring about the decomposition of the hydrosulphite, the amount of moisture it contains and the length of time it is allowed to act may vary within comparatively wide limits without detrimentally affecting the final result. The steaming is carried out in specially constructed "hydrosulphite agers," which allow of a temperature of 102°–104° C. being obtained. For light patterns the ordinary steam at 102° C., and free from air, answers perfectly well; but heavy patterns require more moisture, and to supply this the apparatus is provided with a water trough inside, at the bottom. From the surface of the water aqueous vapour rises and renders the steam sufficiently humid. A printing colour made up with hydrosulphite and the alkaline paste used for the glucose process is given below. It has been used in practice for several years with excellent results.

Dark Indigo Blue 3 per cent.

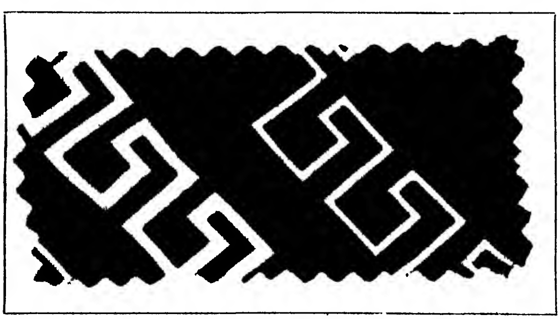
{ 80 grms. hydrosulphite-formaldehyde.
{ 420 „ alkaline thickening. (See Glucose process.)

Dissolve by heat, cool, and add—

150 grms. 20 per cent. Indigo L.L.
350 „ alkaline thickening.

1000

After printing, steam two to three minutes at 102°–104° C. in air-free and moist steam. Then allow to cool and pass directly, in the full open width, into a continuous washing machine supplied with plenty of fresh, cold running water. Wash until all the alkali is eliminated, then sour, wash again, and finally soap, wash, and dry. The printed goods may be allowed to re-oxidise in the air, but this is not necessary except for some heavy patterns printed in very deep colours.



Indigo (Hydrosulphite Process).

More consistent results are obtained by running the goods through one or other of the chrome baths already mentioned (especially in the case of heavy patterns in dark shades), followed by the usual washing and soaping.

The above colour gives a full navy blue when printed on white unprepared

cloth. Lighter shades may be obtained by reducing it with various proportions of a reducing paste containing a little glycerine and about ½ per cent. of hydrosulphite-formaldehyde.

REDUCING PASTE (for light shades).

600	grms.	British gum alkaline thickening.
300	,,	40 per cent. gum Senegal solution.
20	,,	glycerine.
5	,,	sulphoxylate-formaldehyde.
75	,,	water.
1000		

Both Turkey red and Paranitraniline red are easily discharged by the alkaline hydrosulphite colour. For Paranitraniline red discharges, the quantity of hydrosulphite must be increased to 12 20 per cent. according to the depth of the engraving and the intensity of the red ground. For ordinary engraving and an average red (corresponding to a prepare containing 25 grms. β-naphthol per litre) the following Indigo printing paste gives satisfactory results.

INDIGO BLUE 3 per cent. (for Para red).

120	grms.	sulphoxylate-formaldehyde.
100	,,	water.
280	,,	alkaline thickening.
150	,,	20 per cent. Indigo L.L.
350	,,	alkaline thickening.
1000		

Print on Para red dyed cloth, and, after ageing, wash and soap as usual.

Turkey red is discharged by the alkali of the printing colour and therefore does not require any extra addition of hydrosulphite. Better results in every way are obtained when the cloth to be discharged is well soaped in an alkaline soap bath before printing; or a solution of 10–15 grms. of silicate of soda per litre (without any soap) will answer equally well. The only object is to remove surface colour and fatty matters, both of which interfere with the proper action of the discharging agent on the ground colour of the dyed fabric.

On naphthol-prepared cloth the brilliant Azoic colours can be printed along with Indigo and with other colours fixed in the same way, such as the Sulphide colours and the large class of colouring matters known as the Vat dyes.

Most of the members of the several groups of vat colours may be printed according to the foregoing instructions, but, as a rule, they yield far brighter and fuller shades when applied by the methods described in the following pages.

Another artificial preparation of Indigo, not much used at the present time, is Kalle's "Indigo salt" (a bisulphite compound of ortho-nitrophenyl-lactoketone). It is simply thickened and printed on white cloth. The cloth is well dried and padded, either through a mangle or on the printing machine, with caustic soda, which immediately reacts with the pale yellow salt to form a true Indigo blue.

The Printing of Reduced Indigo.—The older processes of printing Indigo in the reduced state, whether as free indigo-white, or as an alkali salt of indigo-white, all possess two inherent defects: one due, as mentioned previously,

to the extreme sensitiveness of the printing colours to air, and the other to the fact that only a relatively small proportion of the Indigo actually printed can be fixed upon the fibre. On the one hand the progressive deterioration of the printing colour, brought about by the rapid and incessant oxidation of its indigo-white content, gives rise to irregularity of shade, the colour becoming weaker and weaker tinctorially as the printing proceeds; on the other hand, since the Indigo is only partially utilised, it is exceedingly difficult to produce a blue of more than medium depth even from very concentrated printing colours. The only conditions under which the approximately complete fixation of Indigo has been effected hitherto, in printing, are those embodied in the glucose and hydrosulphite processes in which the Indigo as such is applied directly to the fibre, and then reduced as quickly as possible, and dissolved and re-oxidised, in contact with the fibre, in such a way as to prevent the undue loss of colouring matter that occurred in earlier processes. For these reasons the printing of reduced Indigo in any form became almost immediately obsolete on the publication of the glucose process in 1883, and for nearly forty years it was regarded as a thing of the past. In a new form, however, it has leaped into prominence again, and, at the present time, is once more a subject of keen interest to Indigo printers.

In 1922 Messrs Durand and Huguenin of Bâle, introduced a product under the name of Indigosol O., which on oxidation yields a true Indigo blue.

Indigosol O. is completely soluble in water and is very stable to air—so much so indeed that, whether in the dry state or in solution, it may be either stored or printed without the slightest fear of premature oxidation taking place. Its application is much simpler than that of any form of Indigo hitherto known. No previous preparation of the cloth with glucose is necessary, nor is any subsequent steaming required, for its reduction; and the absence of strong caustic soda in the printing colour (which consists essentially of colouring matter and ordinary thickening only) obviates the many inconveniences attendant on other methods of Indigo printing. The ease, too, with which perfect white and various coloured reserves can be obtained under Indigosol O. constitutes another great advantage over ordinary Indigo, under prints of which such effects are limited to white and yellow and are, moreover, somewhat difficult to produce successfully.

Indigosol O. may be printed by two different methods, as illustrated in the following formulæ:—

METHOD I.

Printing Colour.

120	grms.	Indigosol O.
250	,,	water at 120° F.
600	,,	starch-tragacanth thickening.
4	,,	soda-ash. Warm to 120° F., cool, and add—
20	,,	Turkey-red oil 40 per cent.

Make up to 1000 c.c.

Print, dry, and pass for 1 minute through the following oxidising bath at 77°–86° F.:—

30	grms.	perchloride of iron 66 per cent.
30	,,	sulphuric acid 96 per cent.
1000	,,	water.

Wash, soap if necessary, and dry. The colour is faster and darker if dried before soaping.

METHOD II.

Printing Colour.

{120	grms.	Indigosol O.
{200	,,	water at 120° F.
550	,,	starch-tragacanth thickening.
4	,,	soda-ash. Warm to 120° F., cool, and add—
{30	,,	nitrite of soda 98 per cent.
{75	,,	water.
20	,,	Turkey-red oil 40 per cent.
Bulk to 1000	c.c.	

Print, dry, and pass, at 77° F., for 1 minute, through—

{ 20 grms. sulphuric acid 96 per cent.
{ 1000 ,, water.

Wash, soap, and dry.

Either of the foregoing formulæ may be applied to the dyeing of plain shades of Indigo by simply substituting water for the greater part of the thickening, and by padding the solution instead of printing it.

Details of the dyeing process, and also of the production of reserve effects under plain shades and printed covers, will be found in the sections devoted to Indigo dyeing and to Reserve styles respectively.

During the last ten years a score or more dyestuffs of the Indanthrene, Algole, Helindone, and Indigoid groups have been converted into compounds analogous to Indigosol O., known collectively as Indigosols. They are described in the section dealing with vat colours (*q.v.*).

Application of Vat Dyestuffs other than Indigo.

The majority of the vat dyestuffs may be mixed with Indigo for the purpose of modifying its shade, or for the production of compound colours, and when used in this way it is obvious that they must be applied by exactly the same methods as are used for Indigo itself.

As a class, however, they are much more susceptible than Indigo to the action of reducing agents, and, for the most part, require also very much less alkali for the solution of their leuco compounds; consequently the composition of their printing pastes differs considerably from that of Indigo.

Many of the Indigoid vat colours are easily reduced with less than a quarter of the amount of reducing agent required for Indigo, and their leuco compounds are generally readily soluble in *weak* alkalies, such as the carbonates of soda and potash.

The anthraquinone derivatives behave in much the same way as regards reduction, but to obtain the best results the reduction must be effected in a caustic soda medium; less caustic soda is usually required than in the case of Indigo, and, in some instances, it may subsequently be converted into carbonate by the addition of sodium bicarbonate, though this is not always feasible.

Again, some vat colours come out well when printed in an almost neutral solution containing potassium sulphite; others are best when reduced with stannous oxide, glucose, or a mixture of stannous chloride and ferrous sulphate, and at least one vat colour can be printed in light shades without any reducing agent at all.

The one property possessed in common by all vat dyes is that of being applied (with more or less success) by means of hydrosulphite-formaldehyde

in conjunction with caustic soda as solvent—in other words, as leuco bodies in alkaline solution. This must not be taken to imply that any one standard recipe is suitable for the printing of all vat colours. Such a recipe, while perhaps perfectly satisfactory for a dozen colours, would most certainly fail to bring out the full tinctorial value of the whole range. In practice quite the reverse obtains; each class of colours has, more or less, its own particular types of recipes, the details of which are modified either according to the requirements of individual members, or in order to adapt them to differences in plant or conditions which may exist in different works.

To deal with the practical application of the vat colours in a rigidly systematic manner is quite impossible; for one colour is frequently applicable by several methods, and, conversely, one method is just as frequently applicable to several colours. Taken altogether, however, it will be found most convenient to treat of each main group separately. In the following résumé, therefore, the processes described are those which have been found, in practice, to be best suited to the majority of the colours in the groups under the headings of which they appear, viz. the *Indigoid*, *Anthraquinone*, and *Sulphurised* groups.

The Indigoid Vat Colours.

This category includes the Ciba series, Durindone series, Thio-indigo series, Helindone series, and the various Brilliant and Brom-Indigos. Although they are all printed in much the same way, the several series present slight differences here and there, and for this reason they demand separate mention in respect of process when such differences are in any way important. In the main, however, they resemble each other so closely that a description of one series is equally a description of the others.

The Indigoid colours, which are all derived from Indigo, Indirubin, or Thio-indigo, constitute a class of dyestuffs characterised by a fastness to light, soap, acids, alkalies, chlorine, and other destructive agencies equal to or exceeding that of such admittedly fast colours as Indigo and the dyed Alizarin reds, purples, and blues, and by a brightness of shade approaching those given by the basic aniline dyes. They may be either dyed like Indigo or printed; they are adaptable to several styles of resist and discharge work; and they can be fixed by either short steaming alone or by the usual prolonged steaming necessary for the ordinary steam colours.

Ciba Colours.—The application of the Ciba (S.C.I.B.) colours, whether by printing or dyeing, depends upon the reduction of the colouring matters, by hydrosulphite, tin oxide, or other suitable reducing agents, to their leuco compounds, which are soluble in alkalies. The alkalinity of the printing pastes is much less than that of Indigo colours, and consequently the Ciba colours are more or less free from the disadvantages that attend the use of Indigo, which, *when used alone*, requires to be applied in the form of a strongly alkaline mixture. It is a remarkable fact, however, that Ciba blue promotes the reduction of Indigo to such an extent that when the two are used in combination for the production of a certain intermediate shade, the Indigo is completely reduced in the presence of *potassium carbonate only*, whereas, in ordinary circumstances, a large amount of caustic soda is absolutely essential to reduce it and fix it properly upon the fibre; in fact its fixation is prevented in proportion as the caustic soda becomes converted into carbonate by absorption of carbonic acid from the air. The percentage of Indigo (20 per cent. paste) on the weight of Ciba blue paste ought not to exceed 30 per cent., otherwise a portion of it remains unreduced, and will be washed out in subsequent processes.

Mixtures of Ciba blue and Indigo—and indeed all Ciba colours—can be effectually fixed in any rapid ager capable of being worked at a temperature of 102° C. No particular precautions are necessary for excluding air, or for maintaining a regular degree of moisture, though, of course, the regularity of the conditions under which the steaming is performed is conducive to regularity of results.

Another great advantage of Ciba colours is that they may be printed along with colours so diverse in properties as Aniline black, the Azoic colours, and almost any of the ordinary "steam colours" like Alizarin red, basic dyestuffs, and the vegetable colours. They withstand the various operations to which these styles are subjected, and it has been proved by experience that they are practically unaffected by either bichromate of potash, mineral acid baths, tartar-emetic, or prolonged steaming.

After steaming, the printed goods are allowed to hang for a short time to re-oxidise. They are then washed in cold water and finally soaped at the boil. This last process is very important: it increases the purity and brightness of the shades, and at the same time increases the fastness of the colours to light and chlorine. A run through a solution of bichromate may be substituted for the hanging of the goods before washing and soaping, but the resulting colours are somewhat duller in appearance.

The printing pastes are exceedingly stable for vat dyestuffs and work well in the machine, as they neither act on the engraved rollers nor attack the doctor edge.

Taken altogether, the Ciba colours as a class are widely applicable in calico-printing. They may be dyed, printed, resisted, discharged; they are well adapted to act as discharge colours on Para red, Para brown, Naphthylamine claret, and as resist colours under Aniline black; they may be printed in conjunction with either oxidation, reduction, or ordinary steam colours; and they may be mixed together in any proportion, or with Indigo and Sulphur colours. In short, for all styles in which fastness is of the first importance—*e.g.* shirtings, dress goods generally, and especially delicately coloured muslin curtains—the Ciba colours are well adapted.

The application of the Ciba colours to resist and discharge styles will be touched upon later. The following are a few of the processes used in direct printing.

In the printing of Ciba colours the use of strongly alkaline pastes, containing a high percentage of caustic soda, such as are essential for Indigo printing, is not necessary; the best results are obtained with potassium carbonate or soda-ash as the alkali, as in the following formulæ, which are applicable to all Ciba colours:—

Ciba Blue 2 B.

{40 grms. Ciba blue 2 B. (mikro-powder).
{60 ,, glycerine.
100 ,, water.
530 ,, thickening G.D.
150 ,, potash (K_2CO_3).

Heat to 140° F., cool and add—

{60 grms. Rongalite C. or Formosul.
{60 ,, water.

1000

THICKENING G.D.

{450 grms. dark British gum (dextrine).
{250 „ water.
{300 „ gum Senegal 50 per cent. solution.

Heat till dissolved, and cool.

For reducing the depth of the above standard colour, additions of the following reducing paste may be made as required:—

REDUCING PASTE.

600	grms.	thickening G.D. above.
{ 50	„	potash.
{ 6	„	Rongalite.
{344	„	water.
1000		

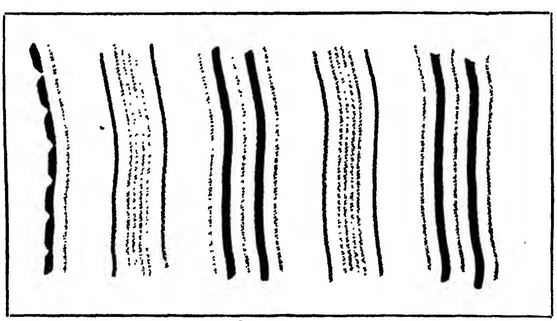
Print on unprepared cloth; steam 2–3 minutes at 102° C.; hang or allow to lie an hour or so, and then, after washing in cold water, soap at the boil in—

2–4	kilos.	Marseilles or other suitable soap.
1–2	„	soda-ash.
1000	„	water.

The strength of the soap is reduced in accordance with the intensity of the shade printed, lighter colours requiring weaker soap.

A run through a hot ½ per cent. solution of bichromate of potash may be substituted for soaping if desired, but the colour becomes greener in tone and loses some of its brightness. A subsequent soaping restores the shade.

Although no *special* precautions need be taken to avoid the presence of air in the steaming apparatus, it must be understood that the less air present the



Ciba Blue 2 B. 4 per cent. and 1 per cent. (S.C.I.B.).

more perfect the result; consequently the regular hydrosulphite agers are the most efficient so long as the temperature is not allowed to exceed 102° C. (216° F.). At a higher temperature the colours are apt to be over-reduced, with a corresponding loss in brilliancy.

Ciba blue may be combined with Sulphur dyestuffs to yield all sorts of compound shades. When mixed with a small quantity of Pyrogene deep black D., for instance, it gives a fine imitation Indigo shade.

Ciba Blue and Pyrogene Black.

A	70	grms.	standard blue A. 50 per cent.	Heat to 120° F. (50° C.), and then add and dissolve whilst stirring—
	448	,,	gum Senegal 30 per cent.	
	320	,,	dextrine paste 50 per cent.	
	100	,,	potash or soda-ash.	
	30	,,	glycerine.	
	20	,,	Formosul.	
B	2·5	,,	Pyrogene deep black D.	Dissolve separately.
	6	,,	caustic soda 66° Tw.	
	3·5	,,	sodium hydrosulphite powder.	
	1000			

The solution of part B would probably be effected more easily by the addition of 100 grms. of water, which could be allowed for by using 348 grms. of a 40 per cent. gum Senegal in place of the quantity of 30 per cent. gum solution given in part A. The standard blue is made as under.

Standard Blue A., 50 per cent.

500 grms. Ciba blue 2 B. paste.

Add gradually to—

120 grms. 30 per cent. gum Senegal.
380 ,, 50 per cent. dextrine paste.

1000

Strain through a hair sieve before use. After printing, proceed exactly as for the previous blue.

By mixing Indigo and Ciba blue in various proportions, intermediate shades are obtained which are characterised by their excellent fastness to light, acids, alkalies, soap, and chlorine. Considering their comparatively small Indigo content, the fastness to chlorine is remarkable, and seems to point to the conclusion that the Ciba blue not only facilitates the reduction of the Indigo in solutions of alkaline carbonates, but also has some further action upon it in the direction of fixing it more permanently upon the fibre ; in fact it seems to play the part of a mordant. Be that as it may, it is indisputable that the Indigo is considerably faster in combination with Ciba blue than when printed by itself. The Alizarins and the direct dyeing colours are well known to combine with the basic aniline colours, and it is not improbable that the Ciba colours possess a similar affinity for synthetic Indigo. The following recipe will illustrate the preparation of a combined Indigo and Ciba blue printing paste. It contains only 3 per cent. by weight of Indigo pure 20 per cent. paste (=0·6 per cent. indigotine), a quantity that under the ordinary conditions would give a light blue very susceptible to the action of dilute solutions of bleaching powder such as are used for the clearing of printed goods. Yet it resists this operation without any appreciable alteration in shade.

Ciba Blue and Indigo.

90 grms. Ciba blue 2 B. paste.
30 ,, Indigo 20 per cent. paste.
620 ,, gum Senegal.
60 ,, glycerine.
140 ,, carbonate of potash.

Heat to 120° F. and add—

60 grms. Formosul.

Dissolve and cool. Print, steam, hang (or chrome), wash, and soap as usual.

Ciba blue is sent out both as a powder and in a paste form. The latter is more convenient, but is rather more expensive for carriage. The other Ciba colours are also made in paste and powder. With the exception of the reds, all the Ciba colours can be printed by the stannous oxide caustic process, but the hydrosulphite process is to be preferred in most cases.

CIBA BLUE (with stannous oxide).

120	grms.	Ciba blue 2 B. paste.
30	,,	stannous oxide 50 per cent. paste.
60	,,	glycerine.
150	,,	British gum (dry).
190	,,	water.
450	,,	caustic soda 90° Tw.
1000		

Allow to stand, and then strain well.

This colour is strongly alkaline, and open to all the objections connected with such colours; but it yields rather darker shades than those resulting from the use of the various hydrosulphites.

The Ciba violets and heliotrope produce very beautiful shades, ranging from full purples to the most delicate lilacs and heliotropes, according to the strength and brand of colour used. Their preparation does not differ materially from that of the blues.

CIBA VIOLETS OR CIBA HELIOTROPE.

Standard.

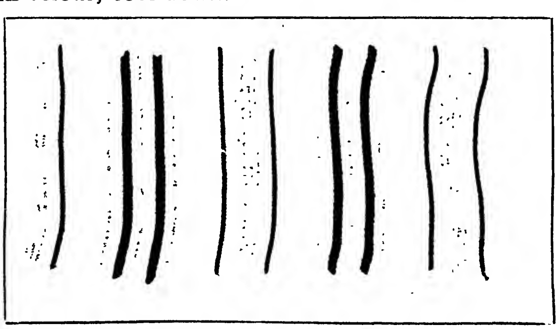
750	grms.	Ciba violet paste or Ciba heliotrope B.
250	,,	30 per cent. British gum paste.
1000		

Strain before use.

Printing Colour.

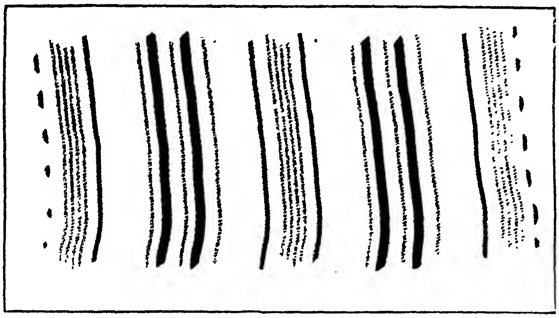
335	grms.	standard.
435	,,	30 per cent. British gum paste.
120	,,	potash or soda-ash.
40	,,	glycerine. Dissolve and add at 120° F.—
70	,,	Formosul.
1000		

When orange in colour, cool down.



Ciba Violet 6 R. paste, 15 per cent.
,, ,, B. Dble. paste, 2 per cent.

Print, dry, steam 2–4 minutes at 102° C., hang, or allow to lie a short time, then chrome and wash ; or, better still, soap for half an hour at the boil with 4/1000 soap solution, containing 2/1000 of soda-ash, which yields the finest, fastest, and most regular shades.



Ciba Violet B. paste, 15 per cent.
„ „ 2 R. Dble. paste, 2 per cent.

Ciba scarlet G. is a bright and very fast red, made up generally like the preceding colours.

CIBA SCARLET G.

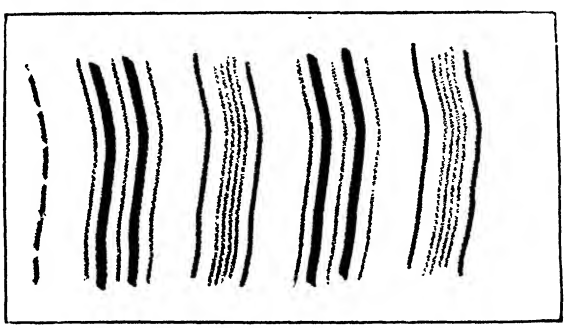
150 grms. Ciba scarlet G. extra paste.
550 „ British gum paste 30 per cent.
50 „ glycerine.
150 „ carbonate of potash.
25 „ sodium hydrosulphite conc. ($Na_2S_2O_4$).

Heat to 140° F., cool, and add—

25 grms. Formosul.
50 „ water.

1000

Print, dry, steam, etc., as above.



Ciba Scarlet G. Extra paste, 15 per cent.
Cibanone Green 5 G. paste, 15 per cent.

In addition to the recipes given above, the following has been found, on the large scale, to give excellent results with the whole range of the Ciba colours. It is simple and convenient, allows of the full effect of the colour being obtained, and, above all, ensures consistency in the matter of the production of compound

shades by the admixture of two (or more) colours—a most important point in practice. Example :—

CIBA PINK.

{150 grms. Ciba brilliant pink B. or R. (20 per cent. paste).
{750 „ K.C. paste.

Mix and add—

25 grms. sodium hydrosulphite conc. ($Na_2S_2O_4$).

Heat to 140° F. until reduced: cool, and add—

{ 50 grms. Formosul.
{ 25 c.c. water.

1000

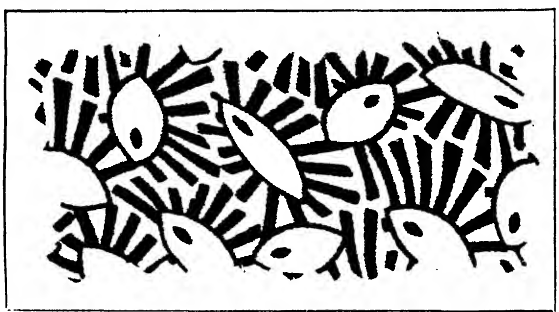
K.C. PASTE.

{125 grms. China clay.
{ 75 „ glycerine.
{250 „ dark British gum.
{300 „ water. Mix, boil, cool a little, and add—
{100 „ potassium carbonate 94 per cent.
{150 „ water.

1000

After printing, steam, chrome, wash, and soap, etc., as already described.

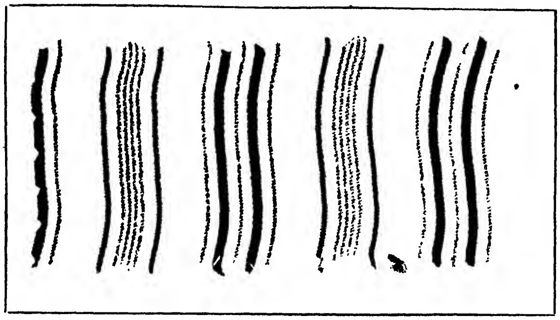
The presence of China clay in this recipe prevents the colours from penetrating too deeply into the fibre, and thus ensures darker shades with an increased brightness due to the white background of bleached cotton shining through.



Ciba Brilliant Pink R., 15 per cent.

An increase, amounting to as much as 30 per cent., in the yield or intensity of vat dyestuffs in general is also effected by the addition of Solution Salt S.V. or Dissolving Salt B. to printing colours containing vat dyestuff, sodium hydrosulphite or sulphoxylate, alkali and a water-soluble di- or polyhydric alcohol, *e.g.* diethylene glycol, glycerine, glycerine oxyethyl ether, thiodiglycol or thiodiglycerol. The alkali salts of the sulphonic acids of benzene, naphthalene and hydrogenated naphthalene, and the sodium salts of carboxylic and hydroxycarboxylic acids of benzene and its homologues, *e.g.* benzoic, salicylic, *o*-cresotic or *o*-toluic acid, produce a similar improvement in depth of shade. Of these various auxiliaries, the two in most general use are Solution Salt S.V. (sodium dibenzylsulphanilate) and Dissolving Salt B. (sodium monobenzylsulphanilate). Solution Salt S.V. is a product of Imperial Chemical Industries, Ltd., and, when dissolved in a suitable medium, say diethylene glycol, is by far the most efficient solvent, to date, for leuco compounds of vat dyestuffs and their sulphonic esters, the Indigosols and Soledons.

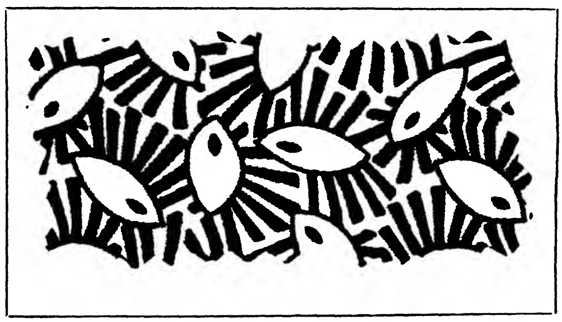
The following pattern may be produced by either of the two last recipes given for Ciba scarlet G. and Ciba brilliant pink B. respectively.



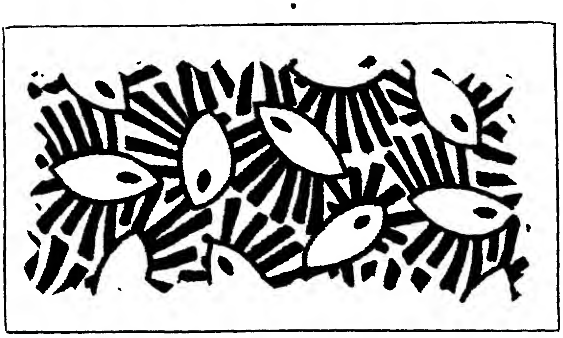
Ciba Red 3 B.N. Ex. paste, 15 per cent.
„ Violet R.N. paste, 2 per cent.

The introduction of two browns of the Ciba type has fulfilled a long-standing requirement of the calico-printing industry for fast vat browns of good tinctorial value, bright in shade, and capable of being applied by the potash-Rongalite process.

Ciba brown G. and Ciba brown 2 R. yield full shades of great fastness to light, soaping, and chlorine, and for these qualities, together with their brightness, they are extensively used in the printing of shirtings, dress goods, and other styles in which fastness is of paramount importance.



Ciba Brown G.



Ciba Brown 2 R.

Ciba Brown.

200 grms.	Ciba brown G. or 2 R. double paste.
655 grms.	K.C. paste (*q.v.*).
25 grms.	sodium hydrosulphite ($Na_2S_2O_4$).

Heat to 140° F. until reduced, cool and add—

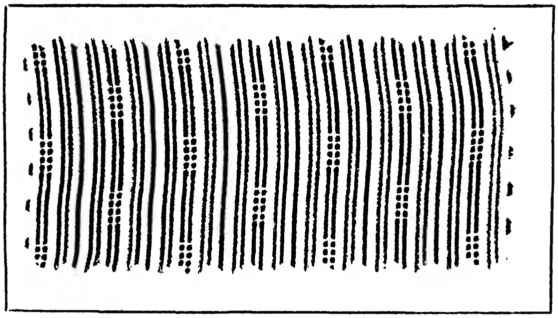
60 grms.	Rongalite (or Formosul).
60 grms.	water.
1000	

Print, dry, steam, etc., as usual.

The several brands of vat printing blacks, manufactured by the Society

of Chemical Industry, Bâle, are applied by methods analogous to those already described. As blacks they find but a limited employment in England but, as illustrated in the pattern, they lend themselves admirably to the production of a useful series of greys.

For printing purposes most Ciba colours are preferably employed in their original paste form; the ordinary dry, powdered colours require very careful preparation to bring them into a fit state for printing, especially if they are intended for light shades which, of course, show up every particle of undissolved dyestuff. Latterly, however, improved qualities of Ciba colours in powder form have been introduced under the name of "Mikro-powders for printing." With these powders a printing colour may be made as quickly and as perfectly as with paste colours and, if reasonable care is exercised, without fear of "specks" developing in the finished print.



Vat Printing Black B.D. paste, 2 per cent.
" " " B.L. paste, 10 per cent.

Durindone Colours.—Like the Ciba colours, the Durindone group consists almost entirely of halogen substitution products of Indigo and Thioindigo, which, for the most part, are identical with the corresponding Ciba colours and are applied by exactly the same means. Thus:—

DURINDONE BLUE 4 B.C.S.

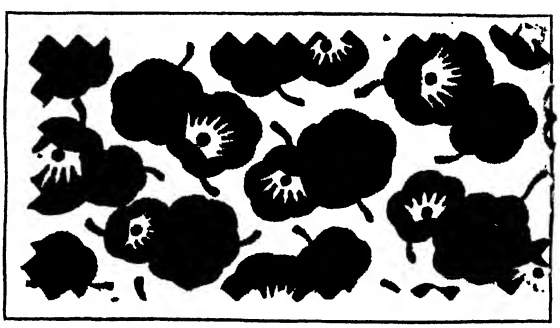
175	grms.	Durindone blue 4 B.C.S. paste.
750	"	K.C. paste (see Ciba pink).
25	"	sodium hydrosulphite conc.

Heat to 140° F., cool, and add—

50 grms. Formosul 1 : 1.

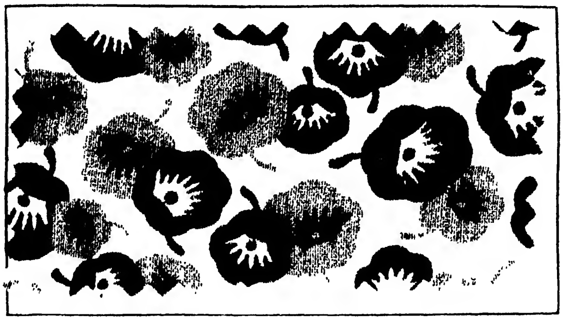
1000

Steam, etc., as usual.



Durindone Blue 4 B.C.S. (I.C.I.).

Other Durindone blues yield greener shades than the above and are not quite so fast.



Durindone Scarlet 2 B. (I.C.I.).

Durindone scarlet 2 B. is a bright colour which, in addition to being useful for direct printing, is largely employed as a discharge colour on tannin mordants—the *vat-tannic* style.

DURINDONE SCARLET 2 B.

200	grms.	Durindone scarlet 2 B. paste.
75	,,	glycerine.
30	,,	water.
50	,,	caustic soda 86° Tw.
490	,,	starch-arabic thickening.
40	,,	sodium hydrosulphite conc. powder.

Heat to 140° F., cool, and add—

70	grms.	Formosul.
45	,,	bicarbonate of soda.
1000		

Steam 4 minutes at 220° F., chrome, soap, and wash.

Durindone red B. (Thio-Indigo 3 B., Helindone red B.) may be regarded as Indigo in which the imino (NH) groups are replaced by sulphur. It is related closely to the ordinary Sulphide dyestuffs, and for light shades may indeed be used as such; for dark shades, however, it requires to be treated as a vat dyestuff.

For a pale pink it is only necessary to use an alkaline thickening and the colouring matter. For red, or rather dark crimson, the addition of a small quantity of hydrosulphite is essential to the production of a full and fast shade. Hydrosulphite may also be added to the weaker colours, but it is not at all necessary.

DURINDONE RED B. (Pale).

a	15	grms.	Durindone red B. paste.
	50	,,	water.
b	100	,,	British gum.
	835	,,	caustic soda 60° Tw.
	1000		

Durindone Red B.

150	grms.	Durindone red B. paste.
100	,,	water.
20	,,	Formosul.
730	,,	alkaline thickening (for Indigo).
1000		

Durindone Red B. (carbonate process).

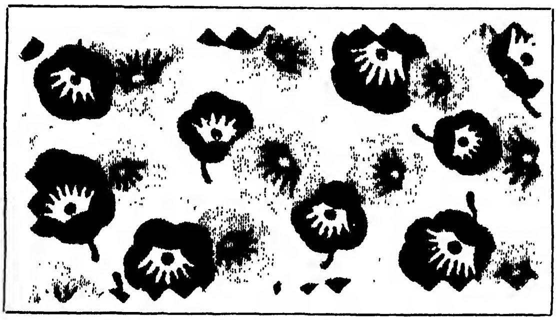
175	grms.	Durindone red B. paste.
775	,,	K.C. paste (see Ciba colours).
15	,,	sodium hydrosulphite conc. powder.

Heat to 140° F., cool, and add—

15	grms.	Formosul.
20	,,	water.
1000		

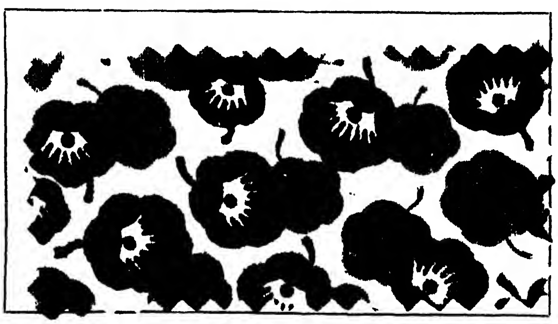
Print on unprepared cloth ; age, chrome, and wash, etc., as for Indigo.

Durindone pink F.F.S. yields a fine bright colour equal in every respect to others of its type. It may be applied by any of the recipes already given for other members of the Durindone and Ciba groups.



Durindone Pink F.F.S. Paste (I.C.I.).

Durindone brown G.S. corresponds exactly with Ciba brown G. and may be printed in exactly the same way.



Durindone Brown G.S. Paste (I.C.I.).

Since the last edition of this work appeared, the group of Durindone colours has been greatly extended. It now includes a full range of colours

equal in quality to other similar ranges. Every member of the series may be printed by the carbonate of potash method, thus avoiding the practical difficulties inherent in caustic soda processes, and the troubles that arise when carbonate and caustic printing colours are worked together in multicolour patterns.

Along with the Durindone blues (tetra-, penta-, and hexabrom-indigos) may be classed the less highly brominated derivatives known as Indigo L.L./R. and Indigo L.L./2 R., which correspond with the old Indigo M.L.B./R. and Indigo M.L.B./2 R. (di- and tribrom-indigo) and Ciba blue B.

Helindone and Thioindigo Colours (M. L. & B.: Kalle).—Some years ago, owing to a trade amalgamation, these two groups of colours, originally distinct, were merged, and they then consisted of substantially the same products which were marketed separately under the old names. Not every member of the Thioindigo group appeared in the Helindone list, nor *vice versa*; on the other hand, many identical colours figured in both lists under different names. The few colours manufactured exclusively by one or other member of the amalgamation were sold by both under different names according to the list from which they were ordered; thus Helindone red B. sometimes passed as such, and sometimes as Thioindigo red 3 B. The same procedure was adopted in the case of every other colour in the two lists.

Since the whole of the German colour-making industry was absorbed in the I. G. Farbenindustrie, further changes in the names of colours have been made, due, partly, to the transference of colours from one group to another and, partly, to the initiation of a policy of systematising the nomenclature. Doubtless this is all to the good; the classification was not perfect, there was a good deal of overlapping, and some groups included members whose properties fell below the general group standard. All the same, it is rather confusing to those who are not in a position to keep pace with the changes; and many users of German colours still persist in ordering them under the old names, with the result that a colour is packed under one name and invoiced under another. Both the Helindone and Thioindigo colours have been subjected to these changes in classification, and the term "Thioindigo" as a group name for a particular range of colours appears to have been dropped by the makers. Be that as it may, it is still constantly employed in the calico-printing trade, and as the Helindone and Thioindigo colours are nowadays identical and interchangeable, a description of the former will serve equally well for the latter.

With two exceptions, all the Helindone colours are derivatives of Thioindigo, or are Indigoid in character. They are quite insoluble in the ordinary solvents, but their leuco compounds dissolve readily in caustic soda, and they may therefore be applied to printing by methods analogous to those employed for other vat colours.

The fastness of the Helindone colours is excellent in all respects. Not only are they fast to washing, acids, alkalies, and light (Helindone scarlet S. is inferior to the rest of the group in this respect), but the majority of them also resist the action of bleaching agents to a considerable extent—a quality which renders them of the utmost value for the production of dress goods, such as muslins, shirtings, blouse materials, etc., all of which are expected to withstand the somewhat drastic treatment meted out to them in most laundries.

As regards the printing of Helindone colours, various methods have been proposed, but the most generally useful is that in which the printing pastes contain, besides colouring matter, the usual ingredients, viz. caustic soda, glycerine, hydrosulphite, and British gum. In some cases the working qualities of the colour are improved by the addition of olive oil, sulphite of potash, and

Dissolving Salt B. (benzyl sulphanilate of soda). In other respects the colours are treated, for the most part, exactly like the Ciba colours, which they closely resemble in general properties.

The chief point to observe, in the successful printing of Helindone colours, is to avoid the employment of too much alkali, since an excess tends to impair the purity and intensity of the shades. Helindone red B.[1] (Thioindigo red B.G.) *may* be printed without any alkali at all, while the other colours require very little.

For the production of full shades of blue of a tone brighter than Indigo itself, the Brom-indigos may be employed along with any of the artificial Indigos. They reduce well with glucose in the presence of caustic soda, and this property enables them to be used either in the ordinary glucose process of Indigo printing, or, in Direct printing, as self colours, in cases where hydrosulphite is not available. On the whole, however, the hydrosulphite method is to be preferred.

In works where the Helindone colours are used along with the Ciba and Durindone series (from which they differ very slightly in properties), the recipes already given may be equally well employed for them. Better results, however, are claimed for the following formulæ:—

	Red.	Green.	Brown.	Blue.
Helindone fast scarlet R. paste	400	..	..	..
„ brown G. paste	..	65	270	..
„ yellow 3 G.N.	..	27	..	..
„ red B. paste	..	..	15	..
Indigo M.L.B./5 B. paste	..	17	..	25
Glycerine	100	100	100	100
Water	40	335	40	511
British gum powder	150	275	250	250
{ Dissolving salt B.	30	20	30	5
{ Water	30	20	30	5
Caustic soda 76° Tw.	60	33	80	15
Hydrosulphite conc. powder	40	13	40	4
Heat until reduced, then cool and add—				
Olive oil	30	30	30	30
Hydrosulphite N.F. conc. 50 per cent. solution	100	30	100	30
Sulphite of potash 90° Tw.	..	15	15	..
British gum paste	20	20	..	25
	1000	1000	1000	1000

After printing, the goods are run twice through the rapid ager at 102° C. for three minutes each time; they are then either soaped at the boil or, alternatively, first rinsed, then chromed (0·2 per cent. solution of bichromate of soda) at 60° C., rinsed again, and finally soaped at the boil.

Helindone scarlet S., Helindone fast scarlet R., and Helindone yellow 3 G.N., when used alone, yield better results if steamed in moist steam at 100°–102° C. Usually, however, the conditions obtaining in the ordinary hydrosulphite ager give sufficiently satisfactory results.

A later addition to the Helindone series is Helindone yellow 3 G., a colouring matter yielding a pure yellow which is fast to light, acids, alkalies, soap, and chlorine.

Helindone yellow 3 G. is best printed in the reduced state with slightly

[1] Buckley, *Jour. of Soc. of Dyers and Colourists*, March 1910, p. 60.

alkaline thickenings, and an addition of Dissolving Salt B. is advisable in order to obtain the best results, both as regards depth of shade and working quality of colour. The makers recommend the following proportions for a full shade of yellow :—

HELINDONE YELLOW 3 G.

150	grms.	Helindone yellow 3 G.
100	,,	glycerine.
60	,,	caustic soda 76° Tw.
30	,,	Dissolving Salt B.
180	,,	water.
200	,,	British gum powder.

Heat at 60° C. and, when a pure blood-red colour is obtained, add—

30	grms.	olive oil.
50	,,	hydrosulphite N.F. conc.
50	,,	British gum solution.
150	,,	sulphite of potash 90° Tw.
1000		

Print and treat the goods as described for other Helindone colours.

Printed according to the foregoing instructions, the Helindone colours give brilliant shades that are exceptionally fast to almost all reagents. They withstand the hydrosulphite discharge process, and consequently may be used for obtaining coloured discharge effects on the Direct colours, Azoic colours, etc.; and, as they resist the action of oxidising agents to a remarkable extent, they cannot be discharged, like Indigo, by the chromate or chlorate method. A notable exception is Helindone grey G.G., which may be discharged with hydrosulphite. Helindone yellow 3 G.N. and Helindone blue 3 G. (and perhaps the above yellow) are derivatives of anthraquinone.

In common with the Ciba series, the Helindone and Thioindigo series include practically every type of pure colour and also shades of grey, brown, and fawn. Bright blues, corresponding to Ciba and Durindone blues, are obtained from the three brands of Indigo M.L.B./4 B., 5 B., and 6 B. (brom-indigos).

Notes on the Indigoid Vat Colours.—From the point of view of a colourist pure and simple, the Indigoid vat colours possess nearly all the qualities that colours are desired to possess. They are easy to apply, they give beautiful shades, they work well in combination, and, above all, they are characterised by great fastness. To some extent their properties debar them from being associated with other classes of colouring matters, but this in itself is no great disadvantage, since it makes it imperative to use them only in conjunction with such colours as will withstand the severe after-treatment that is necessary to develop their full beauty and intensity. In any case it is altogether inexpedient to print multicolour patterns in colours that possess widely different degrees of fastness, and especially is it so when it is quite unnecessary to mix up different classes of colouring matters in a given colour scheme.

Experience has shown that every Indigoid vat colour can be successfully printed by the carbonate process, or a modification of it—a process of great advantage from a practical point of view, since, owing to the absence of *caustic* alkalies, it enables these colours to be applied by a method which is harmless to back greys and blankets ; and also allows of them being used in several of the more usual styles of work of which the after-treatment is given below.

Indigoid colours when printed along with :—

(1) Alizarin, basic, and other steam colours, are first aged at 102° C., allowed to lie a short time, and steamed again for an hour in order to fix the

other colours. The goods are then passed through tartar-emetic, washed, and soaped as usual.

(2) Aniline black: steamed for two minutes at 102° C. and then passed at once into hot bichromate; washed well and soaped.

(3) Insoluble Azoic dyes on β-naphthol containing oxide of antimony: steamed 2–4 minutes at 102° C., allowed to lie a little while, and then well washed, soured, washed, and soaped.

If the Ciba printing pastes have become re-oxidised by long standing, they can be restored to a fit condition for further use by adding 1–2 per cent. of hydrosulphite N.F. conc., and heating gently until the yellowish colour of the leuco compound appears again.

The best Aniline black to use is the Copper sulphide black, containing a little (very little) free hydrochloric acid. The steam colours, too, are better for the addition of a small quantity of extra acetic or formic acid, if they are not sufficiently acid in the first instance to resist the slight alkaline "scum" from the Ciba colours.

The Anthraquinone Vat Colours.

Under this heading are included the Indanthrene, Caledon, Algole, Cibanone, and Alizanthrene groups of vat dyestuffs—all derived from anthraquinone and its various substitution products or from its derivatives benzanthrone and pyranthrone.

The Indanthrene group was the first to be introduced and is yet, by far, the most important, not because the colours in other groups are inferior in fastness and shade, but mainly because it comprises an exceedingly long range of colours of unexcelled printing quality. For many years Indanthrene colours were the only representatives of their class, but, little by little, competitors entered the field and gradually built up the other and smaller groups mentioned above. The colours constituting these smaller groups are generally similar to, and in many cases identical with, the corresponding Indanthrenes, both as regards composition and properties and, other things being equal, may be taken as efficient substitutes for the Indanthrenes. In any case, at the time of writing, some of them *have* to be used in England in order to comply with the "beneficient" tariff laws.

Indanthrene blue S., the first member of an entirely new order of anthraquinone dyestuffs, was discovered by René Bohn in 1901 and put on the market by the Badische Co. Its introduction heralded the commencement of a new era of great importance in the calico-printing industry, and it proved to be the forerunner of a splendid series of vat dyestuffs which, for beauty, brightness, and variety of colour, combined with extreme fastness, are unexcelled. From that time forth new colours of increased fastness have been added to the range in rapid succession until, at the present time, the group comprises upwards of a hundred colours, of which over eighty are specially prepared for printing.

The Caledon group, manufactured by the Imperial Chemical Industries, Ltd., consists of colours of the Indanthrene type. Many of them are identical with the corresponding Indanthrenes, and the series may be said to be of the same general excellence. The discovery of Caledon jade green, by the late Dr J. Thomas of Scottish Dyes, Ltd., stimulated research on the benzanthrone (a derivative of anthraquinone) dyestuffs and has led to important results.

The Cibanone colours (Soc. Chem. Industry, Bâle), with one exception, are not much employed in this country for printing. Cibanone blue 3 G., however, is amongst the fastest of the vat dyestuffs and is used in considerable quantities as a self-colour and also in mixtures for greens and olives. It is very fast to light, soaping, and chlorine.

The Algole colours form a subsidiary group to the Indanthrenes. They are not generally considered to be quite so fast as other Anthraquinone colours but, in effect, they are of excellent all-round fastness and are well adapted for the production of fast styles which are not required to fulfil the conditions demanded in the case of "guaranteed fast" work, like the best shirtings. In any case, as a class they are a great deal faster than the best steam mordant colours.

The Alizanthrene group is now combined with the Caledon group except for, perhaps, one colour—Alizanthrene navy blue, which corresponds to Hydron blue.

Since the formation of the I. G. Farbenindustrie, a similar regrouping of the vat dyes of the several allied firms has been carried out.

Members of the Algole, Helindone, Hydron, Thioindigo, Alizarin-Indigo and Leucol groups have been reviewed, and those which proved to be up to the Indanthrene standard were transferred to that group and renamed. The rest were also re-arranged, most of them becoming Algoles, and advantage was taken to drop some of the weaker members altogether. The Indanthrene group, therefore, does not now consist entirely of true Indanthrenes, but it does consist of colours which conform to the high standard connoted by that designation.

General Properties.—As at present constituted into groups of selected colours not falling below a certain standard of excellence, the Anthraquinone colours, as a class, are fast to acids, alkalies, boiling soap, and chlorine, and their resistance to light is, in general, excellent, none being less than good in this respect. Under the action of chlorine and other strong oxidising agents several colours (notably some of the blues) change in shade without being actually destroyed, the original colour being restored either by an energetic soaping or by a short passage through a solution of sodium hydrosulphite, followed by washing and re-soaping. The original brands of Indanthrene, Caledon, and Cibanone greens are converted into very fast blacks or greys by the action of bleaching powder, the depth of shade depending upon the original strength of the colour. By careful selection a group of Anthraquinone colours can be got together which resists perfectly acids, alkalies, soap, light, and chlorine; and as this group includes various shades of red, blue, yellow, green, violet, orange, brown, and black, it permits of almost any desired combination of colours being obtained of consistent fastness throughout. Many of the Indanthrene and Caledon colours, in addition to possessing the foregoing qualities, also withstand the processes of hot and cold vulcanising and other somewhat drastic operations connected with the production of mackintosh goods and other waterproofed materials such as awnings, cart-sheets, and tent cloths. In short, the Anthraquinone colours are practically indestructible by any of the agencies to which prints are usually subjected—at all events, they are as permanent as the cloth upon which they are printed or dyed.

In their practical application the Anthraquinone colours present certain inconveniences which, in spite of their remarkable fastness and beauty, have had the effect of limiting their use for printing purposes. In the first place their very fastness has its drawbacks, for if the goods are damaged in process it is almost impossible to bleach out the colours sufficiently well to allow of reprinting. Then, again, the back greys (as is unavoidable in ordinary printing machines) always receive a certain amount of colour along each side, and this colour, even if it be not developed in the usual way, becomes more or less fixed on the fibre, and is productive of many difficulties during the subsequent bleaching. Something may be done to rectify this by boiling under pressure with caustic soda and Leucotrope, but the result is by no means invariably satisfactory.

Another difficulty, experienced in some quarters, is that the Anthraquinone colours are not too easy to apply ; they are not fool-proof and, unless certain precautions are observed and a reasonable amount of supervision exercised, they are apt to yield disappointing results. Undue exposure to air, or to acid vapours, after printing and before steaming, either prevents the development of the colour altogether or is productive of weak and uneven shades ; variations in steaming conditions (time, temperature, and humidity) also operate in the same direction ; and exposure to bright light (after steaming) whilst the printed colours are still in the leuco state, or only partly re-oxidised, generally results in the colouring matter being more or less destroyed. This last effect is particularly noticeable in colours of the Indanthrene blue G.C.D. type, which are rapidly destroyed by the action of bright light even during the process of re-oxidation with bichromate or perborate of soda. Once fixed, however, under proper conditions, they are amongst the fastest colours known.

An objection occasionally advanced against the use of Anthraquinone dyestuffs is that they yield their fullest depth of shade only when reduced in a strongly *caustic* medium. To some extent this is true, but it is less true to-day than it was when the Indanthrene colours were first put on the market. Improvements in dyestuffs, processes, and machinery have made it possible to substitute carbonate of potash for caustic soda, with results that differ so slightly, in most cases, as to be negligible. Caustic alkalies are to be avoided wherever possible. They utterly destroy woollen printing blankets and in addition to mercerising the cloth that is being printed—causing it to shrink in both length and width—they also mercerise the back greys with disastrous results if these are ultimately destined for steam colours or dyed work. They are unpleasant to deal with in bulk and dangerous if they come in contact with the skin, causing sores ; and machines upon which they are printed have to be washed down from top to bottom before they can be used for ordinary work. Hence the preference for carbonate of potash as the alkali component of vat printing colours. It certainly overcomes the mercerising difficulty and if, at times, it yields slightly lighter shades, the cost of adding a little extra colouring matter is more than counterbalanced by the gain in other directions.

The question of the fixation of undesirable colour on the back greys has also received attention. By preparing the greys in solutions of such substances as Leucotrope, Ludigol, various ammonium salts or mixtures of chlorates with organic acids—all of which act as *resists*—it is possible to prevent the fixation of practically any vat colour upon the fibre.

These preparations, however, add considerably to the cost of production, and for this reason they have not found any general application in practice.

The difficulties and inconveniences which, until recently, have surrounded all methods of printing Anthraquinone colours have caused them to be regarded somewhat unfavourably, with the result that their use has been restricted to the execution of special styles only. One, indeed, of the original methods, and that the best so far as depth of shade is concerned, is free from the defects of mercerising and fixation of colour on the back greys ; but it depends on the after-development of the print by a passage through strong caustic soda, and demands so much supervision, is so delicate and difficult to work satisfactorily in bulk, and, in addition, does not fall into line with usual works practice, that it is rarely employed on the large scale.

The disadvantages attendant on the printing of strongly caustic colours disappear almost entirely when the printing machines are fitted up with mackintosh wash-blankets. These blankets resist for a long time the action of caustic soda, and, no back greys being used, there is nothing to damage.

The Anthraquinone colours come into the market in the form of pastes and powders which are soluble in alkaline solutions of reducing agents, and their application to direct printing depends upon this property of being reduced, and subsequently re-oxidised, in a manner analogous to Indigo and the Indigoid colours. In practice, the reduction is effected in different ways according to the conditions under which the colours are to be applied. The darkest shades are obtained by the caustic soda method (without steaming), using iron and stannous salts as the reducing agents. For blotches, or heavy objects, the colour is reduced by a short steaming, using either stannous oxide or sulphoxylate-formaldehyde and caustic soda, soda-ash, or carbonate of potash, as reducing agents; and in special cases the glucose process may be employed to advantage, though it does not yield the brightest or fullest shades.

The addition of naphthols increases the depth, beauty, and evenness of light and medium shades of the Anthraquinone colours, so that these colours are admirably adapted to the production of fast multicolour effects in combination with any of the Azoic colours. Like the Indigoid colours, too, the Anthraquinones will, under certain conditions, withstand prolonged steaming—an advantage which allows of their being associated with the ordinary steam colours, *e.g.* Alizarin, Persian berries, and other mordant dyestuffs, as well as basic colours; and, in common with the rest of the vat dyes, they can be printed along with almost any colour that is developed by a short steaming, as, for instance, Aniline black, Diphenyl black, Paramine brown, the Sulphur colours, etc.

Application.—For the more convenient description of their methods of application, the Anthraquinone colours have been divided into two main groups, viz.: (1) the Indanthrene, Alizanthrene, Caledon, and Cibanone series; and (2) the Algole and Alizarin-Indigo series. Both series may be applied by exactly the same methods, but better results are obtained by working according to the special processes given below.

The printing of the Indanthrene, etc., group on cotton is usually carried out by one or other of the following processes:—

(1) THE CAUSTIC SODA METHOD (without steaming).—In this process, which gives the darkest colours, and is especially suitable for fine shirting and cover patterns, the colouring matter, mixed with tin crystals, sulphate of iron, tartaric acid (optional), and a suitable thickening, is printed on white unprepared cloth, and the goods, after well drying, are passed in the open width through a hot solution of caustic soda. The hydrates of tin and iron (more particularly the iron) thus formed reduce the colouring matter to its leuco compound, which, in dissolving in the alkali, penetrates into the body of the cloth, where it is subsequently re-oxidised and fixed as an insoluble colour.

For the preparation of the printing pastes the proportions of the various ingredients, as given by the makers, are as follows:—

Dark.	*Medium.*	*Light.*	*Pale.*		
200	100	50	25	grms.	colouring matter.
120	60	30	30	,,	ferrous sulphate.
20	10	5	5	,,	stannous chloride.
100	100	50	25	,,	tartaric acid.
560	730	865	915	,,	thickening.
1000	1000	1000	1000		

The tartaric acid, finely ground, is first of all dissolved in the thickening; the stannous chloride is then added, and lastly the ferrous sulphate, which may

be dissolved in a sufficiency of water, used in place of a portion of the thickening if this latter is made thick enough at the outset to allow of water being introduced. The whole is well stirred until the salts are completely dissolved, and it is then added gradually to the dyestuff whilst stirring with a stiff wire brush, which is the best means of avoiding specks.

When thoroughly incorporated and quite smooth, the colour is well strained and printed in the ordinary way. The goods may be dried either over steam-heated cylinders or in a hot-air apparatus.

The fixation of the colour is effected by passing the perfectly dry printed goods through a beck containing a solution of caustic soda 30° Tw. at a temperature of 160°–175° F. The treatment lasts about 30 seconds. In order to prevent the soiling of the "whites," which is liable to occur if a number of printed pieces are passed continuously through the same caustic bath, it is recommended to add 1–10 volumes of "manganese paste" (according to the quantity of colour on the goods) to every 100 volumes of caustic soda in the beck. The manganese paste is prepared by precipitating manganese chloride with caustic soda and bleaching powder. Thus:

$$\left\{\begin{array}{lll} 7\cdot5 & \text{kilos.} & \text{manganese chloride } 72^\circ \text{ Tw.} \\ 17\cdot5 & ,, & \text{water.} \end{array}\right.$$

Add—

6·25	,,	caustic soda 53° Tw.
20	,,	bleaching-powder solution 12° Tw.

Mix well before use.

On emerging from the hot caustic bath, the goods must not be squeezed, but given a short run through the air to cool down, and then passed directly into cold caustic soda, out of which they may be passed between squeezing rollers without any fear of the colour marking off. They are then passed into a series of washing becks furnished with "spirt pipes" or sprays, and plenty of clean cold water, followed by a run through sulphuric acid $4\frac{1}{2}$° Tw., another good wash, and finally a soaping at 175°–212° F. In the case of all but the lightest colours it is advisable to allow the goods to lie in the sulphuric acid for some time before they are finally washed and soaped, the object being to remove thoroughly all traces of iron, which, if allowed to remain, would oxidise to yellow ferric oxide, and thus dull the colours. When the colour used contains more than 10 per cent. of dyestuff the goods are allowed to steep in 3 per cent. sulphuric acid for an hour; if it only contains 10 per cent. or less, it is sufficient to saturate the goods in the acid, and then (without squeezing) allow them to lie in pile for about the same period. They are then washed and soaped. The whole series of operations, up to and including souring, are best conducted on a continuous machine or in an open soaper, one compartment of which is left empty to provide the airing mentioned above, after the treatment in hot caustic soda.

For fine patterns printed in dark and medium shades of Indanthrene colours it is best to use a starch and British gum thickening, or a British gum thickening alone. For lighter shades and heavy patterns a mixture of British gum and gum Senegal is recommended; but gum Senegal alone gives the brightest and most even prints; and although the colours yielded are lighter than with other thickenings, it is advisable to use gum Senegal wherever its price will allow. By itself, starch gives the darkest colours of all, but its employment is restricted, and in general, for any kind of fine pattern, it is mixed with British gum.

BRITISH GUM PASTE.

450	grms.	British gum.
550	,,	water.
1000		

Boil and cool.

GUM SENEGAL THICKENING.

500	grms.	gum Senegal.
500	,,	water.
1000		

STARCH—BRITISH GUM PASTE.

225	grms.	British gum.
75	,,	wheat starch.
700	,,	water.
1000		

Boil and cool.

In the after-treatment of Indanthrene and allied colours by the caustic soda (without steaming) process, it is of the *utmost importance* to wash out all the caustic soda in the printed pieces as soon as possible after development. If the goods containing dilute soda are exposed to the air for any length of time, the colour not only loses in brightness and depth, but also becomes irregularly developed. For this reason it is preferable to perform all the operations following the printing in a continuous manner, as by so doing the last traces of alkali are effectually neutralised in the final *sour* beck, which must be kept up to the proper degree of acidity by additions of fresh sulphuric acid at regular intervals.

By the foregoing method, and according to the foregoing recipes, practically all members of the following colour groups may be applied equally well:—

Indanthrene.	Caledon.
Alizanthrene.	Hydranthrene.

When printed in conjunction with Aniline or Diphenyl black the above printing colours are used for the production of fine and exceedingly fast shirting and blouse prints. With the exception of a short steaming in the ordinary rapid ager, the treatment of the printed goods is exactly as described above.

(2) THE STEAMING METHOD.—This process is suitable for all the Indanthrene groups of colours mentioned above.

The reduction of the colouring matter is brought about by the action of *stannous oxide* in presence of caustic soda, and under the influence of hot air-free steam. For pale colours the ordinary 2–3 minutes' steaming is sufficient, but dark colours are improved considerably by a longer steaming, or by being steamed twice. In any case the steam ought to be as free from air as possible, and the supply pipe and ventilating arrangements ought to be such as will ensure the constant supply of fresh steam.

The various shades of printing colours are prepared in much the same way as for the preceding process, viz.—

Dark.	*Medium.*	*Light.*	*Pale.*	
200	100	50	20 grms.	colouring matter.
80	40	25	25 ,,	stannous oxide paste 50 per cent.
50	50	30	30 ,,	glycerine.
670	600	600	600 ,,	alkaline thickening B.S.
..	210	295	325 ,,	dextrine and Senegal paste.
1000	1000	1000	1000	

The oxide of tin is added to the colouring matter, and well stirred in with a steel wire brush to break up any lumps of either; the other ingredients are then added in the above order, and the whole, after well stirring, is strained and printed.

The addition of 50–100 grms. of a 30 per cent. alcoholic solution of β-naphthol to every 1000 grms. of light and medium printing colours increases the depth of shade and promotes regular development of the colour. It therefore enables a smaller amount of dyestuff to be used, and at the same time improves the quality of the work. For fine patterns the addition of naphthol is unnecessary.

After printing, the goods are steamed in the rapid ager for from 5–10 minutes according to the intensity of the shade printed; they are then immediately washed in the full open width, passed through dilute sulphuric acid (1 part acid 168° Tw. to 1000 parts water) to neutralise the last traces of soda, well washed again, and finally soaped at 175° F.

The stannous oxide and alkaline thickening are prepared as follows:—

Alkaline Thickening B.S.

300 grms. 60 per cent. British gum paste.
350 ,, 50 per cent. gum Senegal.

Add to this gradually *in the cold*—
1350 grms. caustic soda 90° Tw.

2000

Stannous Oxide 50 per cent.

150 grms. stannous chloride.
20 ,, hydrochloric acid 30° Tw.
600 ,, cold water.

Dissolve and add gradually whilst stirring—
70 grms. soda-ash in
600 ,, water.

Wash the precipitated oxide with water by decantation and then filter it to a 50 per cent. paste.

If desired, the above method of preparing steam colours can be modified by using sulphoxylate-formaldehyde in place of the tin oxide. The results obtained are practically identical; but whether tin oxide or Rongalite is used, the colours, whilst pure and fast, are not so deep as those obtained by the caustic soda-tin-iron method.

In case a proper hydrosulphite ager is not available for the steaming, and an ordinary type of Mather & Platt machine has to be used, the quantity of tin oxide (or of sulphoxylate) must be increased in order to counteract the oxidising action of the air which enters the steaming chamber through the inlet and outlet slits of the machine.

By this process of applying Anthraquinone colours it is possible to obtain

combined effects by printing *light shades* of them on β-naphthol-prepared cloth, along with any of the diazo printing colours. The longer steaming, however, that is necessary for the full development of dark and medium shades is detrimental to the Azoic colours; so that when these latter are intended to work in the same pattern as vat colours, it is preferable to adopt the preceding process, viz. the caustic soda-tin-iron method.

(3) THE SODA-ASH METHOD (with steaming).—The only difference between this method and the one described last is that soda-ash is employed as the alkali, in place of the more energetic caustic soda. In other respects the two methods are identical, at least in so far as the preparation of the printing colours and the after-treatment of the cloth are concerned.

For dark, full shades in outlines and small objects, it is always best to use the *caustic soda steaming process*, but for the production of light shades and medium blotches of the greatest uniformity the soda-ash process can be employed with advantage. Moreover, the weaker alkalinity of the colours renders them more suitable for printing in combination with Aniline black; and they can also be printed along with the ordinary steam colours—Alizarin, etc.

The reducing agent employed may be either stannous oxide or sulphoxylate according to circumstances. The choice of the most suitable will be determined by the results of practical trials made with a view to utilising existing plant to the best advantage. For an ordinary rapid ager working under the best conditions, *i.e.* with a copious supply of air-free steam, the stannous oxide will usually yield more satisfactory results than sulphoxylates of any brand; but with the modern high-temperature agers, sulphoxylate, etc., will leave little to be desired in the way of good, fast colours.

According to the particular conditions obtaining, then, either of the following reducing pastes may be used:—

REDUCING PASTE I.

100	grms.	soda-ash.
230	,,	water.
475	,,	British gum and Senegal thickening.
100	,,	glycerine.
45	,,	sulphoxylate-formaldehyde.
50	,,	water.
1000		

or

REDUCING PASTE II.

100	grms.	soda-ash.
200	,,	water.
450	,,	British gum and Senegal thickening.
100	,,	glycerine. Dissolve, cool, and add—
50	,,	stannous oxide paste 50 per cent.
100	,,	30 per cent. alcoholic sol. of β-naphthol.
1000		

The printing colours consist of—

10–120	grms.	of colouring matter.
990–880	,,	reducing paste I. or II.
1000 1000		

After printing, the goods are steamed 5–7 minutes in air-free steam, then thoroughly washed and soured in sulphuric acid at $\frac{1}{5}$° Tw. (about 1 : 850). For very light shades a short steaming of 3–4 minutes is often sufficient; darker shades require the full 7 minutes, and in all cases the longer the steaming the deeper the colour.

Compound shades may be made by mixing suitable colours according to the well-known principles of colour-mixing.

In all processes for Anthraquinone colours, the steaming and washing ought to be proceeded with as soon after printing as possible. Prolonged exposure to the air, either before or after printing, is certain to result in irregularity in the colours of the finished goods.

Taken altogether, therefore, the employment of Anthraquinone colours is best restricted to styles that can be handled quickly, *i.e.* those of which the colours are fully developed by a short run through one or other of the various types of rapid steam agers.

(4) Glucose Process.—It has been found possible to print these colouring matters on glucose-prepared cloth in the same way as Indigo; and although one of the preceding three methods is to be preferred wherever it can be applied, it is not unlikely that the glucose process will prove to be a valuable alternative method in many cases—as, for instance, in the alkaline discharging of Turkey red, for the production of a brighter green than can be obtained from a mixture of Chrome yellow and Indigo, which latter is a dull blue compared with Indanthrene blue R.S. or G.C.D., etc.

The best results are obtained by steaming for 2–3 minutes in an ordinary Indigo steamer, whereas for Indigo itself $\frac{1}{2}$–$\frac{3}{4}$ minute is sufficient. The difference between the longer and shorter steaming is very pronounced, the shades produced by the former being twice the depth of those produced by the latter. Probably a still longer steaming would further improve the colours as regards their intensity.

A comparison of the results obtained by the glucose process with those by the stannous oxide method shows that the latter is, in general, the more advantageous.

The colours prepared in the following way are printed on cloth prepared as for Indigo in a 20–30 per cent. solution of glucose and carefully dried.

Printing Colour.

100	grms.	colouring matter.
50	,,	glycerine.
700	,,	alkaline thickening for Indigo.
150	,,	gum-dextrine thickening.
1000		

Print, dry carefully, and then steam at once for 2–3 minutes in damp air-free steam. The steaming is done in either the special Indigo steamer or in the ordinary ager. After steaming, wash in plenty of fresh cold water, and finally soap at 180° F.

(5) The Potash-Rongalite and Bicarbonate Methods of Printing Indanthrenes, Etc.—As already noted, it was formerly considered that only medium and light shades of Indanthrene colours could be printed by the potassium carbonate process and that the fullest yield of colour was obtainable only by printing mixtures containing a high percentage of free caustic soda. In some instances, notably that of Indigo, that may still hold good, but it is

nevertheless a fact to-day that the caustic soda processes for printing all other vat dyestuffs have fallen into disuse. Occasionally the original caustic soda developing process is still employed in small works where no suitable steaming apparatus is available, but otherwise the caustic alkali methods are obsolete as general processes for direct print-on styles, though still useful for discharge styles on tannin mordants.

The potash-Rongalite and bicarbonate processes, neither of which is new, were for a long time practically confined to the printing of Indigoid dyestuffs but, with the many improvements that have been effected during recent years both in ageing and steaming machines and in the physical condition of the colouring matters themselves, they have now become also the standard methods of printing Indanthrenes and similar dyestuffs.

The extremely fine state of division in which these dyestuffs exist in present-day paste and powder forms (specially prepared for printing) allows of them being easily reduced to their alkali-soluble leuco compounds, and printed successfully, in the presence of alkali carbonates alone, no caustic alkali being either present or necessary in the finished printing colour.

The difference between the two methods is one of procedure rather than of principle. In the potash-Rongalite formula the printing colour consists essentially of dyestuff, reducing agent, thickening, and potassium carbonate; in the bicarbonate formula the colouring matter is first reduced in the presence of a minimum of caustic soda, which is afterwards converted into the normal carbonate by the addition of a calculated amount of sodium bicarbonate. The final result is the same in both cases—at least in so far as the nature of the alkalinity is concerned—*i.e.* neither printing colour contains any free caustic alkali.

All the printing brands of the Indanthrene and Caledon groups, and most other Anthraquinone colours, are satisfactorily reduced, in steaming, by Rongalite and potash alone; a few are preferably pre-reduced (in the printing colour) with sodium hydrosulphite, in which case sufficient Rongalite is added to compensate for any premature re-oxidation that may occur whilst the goods are in process; and yet others, especially the powder brands, not usually recommended for printing, yield the best results when pre-reduced in the presence of caustic soda followed by an addition of bicarbonate, as already mentioned.

Any of the Indanthrene colours, specially prepared for printing, whether in paste or powder form, are applicable by any of the foregoing variants of the carbonate process, the choice of any particular method being dictated by considerations of works' conditions and of the nature of the colouring matter employed.

Various assistants, such as Dissolving Salt B (benzyl sulphanilate of soda), Glyecine A., and phenolates and naphtholates may be added to the printing colour in cases where their inclusion has been found to facilitate the reduction of the dyestuff and to increase its fixation. With the "Suprafix" brands of Indanthrene dyestuffs, which possess exceptionally good fixing properties, such additions are superfluous and, in some instances, even detrimental.

Application.—Though the individual members of the several groups of Anthraquinone dyestuffs represent various substitution products of different derivatives of Anthraquinone, they all possess the common property of being fixed by similar methods. Hence, the following description of the methods employed in the printing of Indanthrene colours will illustrate equally well the application of analogous colours in the Caledon, Algole, and Cibanone groups.

(A.) Indanthrene Colours in Paste.

Standard Colours.

Recipe.	I.	Ia.	Ib.
	grms.	grms.	grms.
Indanthrene dyestuff in paste or double paste, fine	75–300	75–300	75–300
Glycerine	80–100	40–50	80–100
Glyecine A.	..	40–50	..
Dissolving Salt B.	..	..	30–30
Starch-tragacanth paste	500–380	500–380	500–350
Potassium carbonate	80–120	80–120	80–120
Rongalite C. or Formosul	60–100	60–100	60–100
Water	205–0	205–0	175–0
	1000	1000	1000

Reducing Pastes for above.

Recipe.	I.	Ia.	Ib.
Crystal gum or British gum thickening	650	650	650
Glycerine	50	25	50
Glyecine A.	..	25	..
Dissolving Salt B.	..	..	15
Potassium carbonate	50	50	50
Rongalite C. or Formosul	40	40	40
Water	210	210	195
	1000	1000	1000

In making up printing colours according to these recipes, the Rongalite, potassium carbonate, and dissolving salt are first mixed with the water or thickening and dissolved ; the other ingredients are then added and the whole stirred up and allowed to stand overnight before use. A certain amount of reduction takes place during this period of standing, and darker and more uniform shades are obtained than if the colours were printed immediately after making-up.

In the case of the following colours :—

Indanthrene Blue R.S., double paste fine,
,, Brilliant Blue R., double paste fine,
,, Brilliant Green 4 G., ,, ,, ,,
,, Grey 3 B., ,, ,, ,,
,, Brilliant Blue 3 G., paste fine,
,, Brilliant Green G.G., ,, ,,

it is advisable to dilute the colour paste with half to an equal quantity of water before adding it to the thickening paste, otherwise irregularities arise.

In the printing of certain Indanthrene blues (and the corresponding Caledon

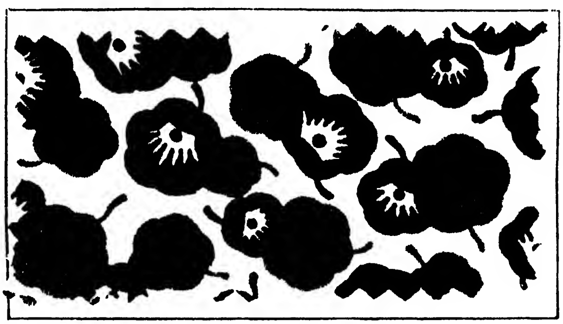
colours) the quantity of Rongalite must be reduced so as not to exceed two-thirds of the weight of dyestuff in the form of double strength paste or one-third in the form of ordinary paste. Thus:—

75–120 grms. Indanthrene blue G.C.D. double paste require only 50–80 grms. of Rongalite.
75–120 grms. Indanthrene blue B.C.D. double paste require only 50–80 grms. of Rongalite.
75–120 grms. Indanthrene blue R.S. double paste require only 50–80 grms. of Rongalite.
75–120 grms. Indanthrene brilliant blue R. double paste require only 50–80 grms. of Rongalite.
150–240 grms. Indanthrene brilliant blue 3 G. ordinary paste require only 50–80 grms. of Rongalite.
150–240 grms. Indanthrene blue F.R.S. ordinary paste require only 50–80 grms. of Rongalite.

per 1000 grms. of printing colour.

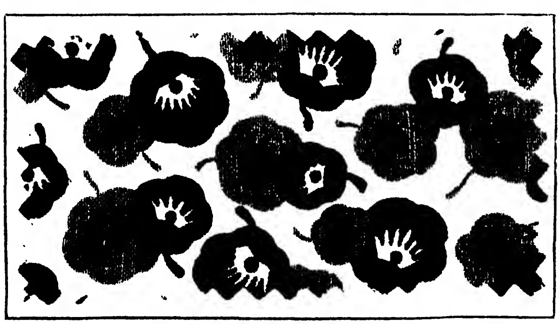
If these proportions are exceeded, the shades of the above colours are liable to be dulled, becoming greyer in tone, especially if steamed in rather dry steam.

The following printed patterns illustrate the application of the foregoing recipes which, of course, are as suitable for the colours shown as for the Indanthrenes.



Caledon Blue G.C.P.S. (I.C.I.) (Indanthrene Blue G.C.D.).

Caledon jade green is one of the fastest colours known. It was invented in England and, later, was manufactured under licence in Germany.

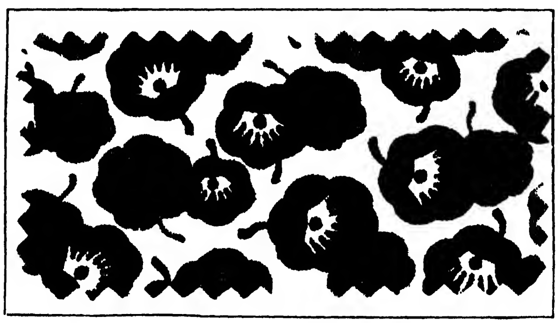


Caledon Jade Green X. 200 (I.C.I.) (Indanthrene Brilliant Green F.F.B.).

Caledon yellow G. represents an improved quality of one of the earliest Indanthrene yellows.

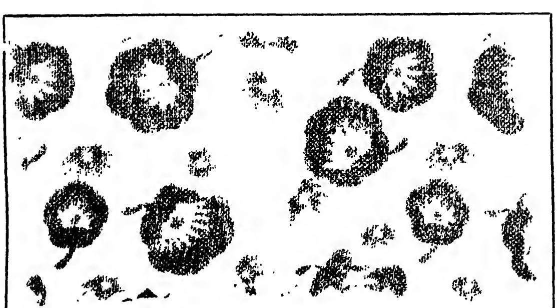
Caledon Yellow G. 200 Paste (I.C.I.)
(Indanthrene Yellow G.).

The Caledon brilliant purples 2 R. and 4 R.S. are largely used in the fast "guaranteed" trade both as self-shades and in mixtures.



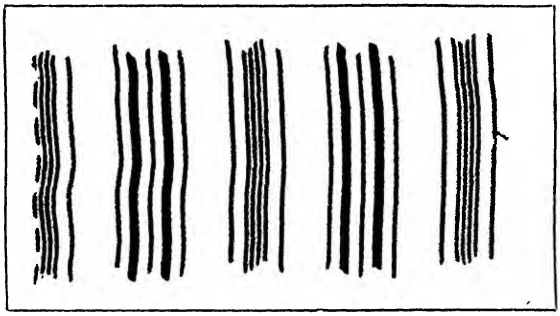
Caledon Brilliant Purple 2 R. 200 Paste (I.C.I.)
(Indanthrene Brilliant Violet 2 R.).

Caledon gold orange G.S. is a bright orange, yellowish in tone, which finds considerable employment in most assortments of "guaranteed" styles.



Caledon Gold Orange G.S. 200 Paste (I.C.I.)
(Indanthrene Printing Orange G.O.).

With the exception of the two blues illustrated in the pattern below, the Cibanone range of Anthraquinone colours finds but little employment in textile printing.



Cibanone Blue 3 G. (S.C.I.B.) Dble. Paste, 150 grms. per kilo. of printing colour.
„ „ 3 G.F. „ „ „ 30 „ „ „ „ „ „

Cibanone blue 3 G. is, however, an important colour and was, for a long time, the only fast greenish-blue available; it was practically indispensable for the production of bright greens before the advent of colours of the Caledon jade green type. Cibanone blue 3 G. is the prototype of Indanthrene blue green F.F.B. Other members of the Cibanone group are best applied in printing by one of the following pre-reduction processes—preferably by Recipe II*a* as described under (C.) Ordinary Powder Brands of Indanthrenes—or by a caustic soda process.

Pre-reduction Method.—In the event of colours being required for printing immediately after preparation, it is advisable to employ the following variation of the foregoing potash-Rongalite recipes. By this method the dyestuff is *pre-reduced* with hydrosulphite ($Na_2S_2O_4$) and either potassium or sodium carbonate, and is at once in a fit state for printing; prolonged standing is avoided and, in several cases, brighter and fuller prints are obtained.

PRE-REDUCTION METHOD.

100–250 grms. Indanthrene dyestuff (paste).
80–100 „ glycerine.

Mix and add—
430–380 „ starch-tragacanth paste.
80–120 „ potassium carbonate (or 50–60 grms. soda-ash).
15–30 „ sodium hydrosulphite.
Heat to 130°–140° F. for 20–30 minutes.

Cool to 120° F. and add—
50–75 grms. Rongalite or Formosul.
245–45 „ water.

———
1000

Reducing pastes as for recipes (I), (I*a*), and (I*b*) (page 376).

In the case of those dyestuffs which yield better results with Dissolving Salt B. or Glyecine A. the requisite amounts of these assistants are added to the above printing colour (see note (6), page 386).

The pre-reduction method gives brighter and darker prints with the dyestuffs noted below :—

Indanthrene Printing Violets R.F., B.F., and B.B.F.
„ „ Red B.
„ „ Brown R. (best with soda-ash).
„ Brilliant pink B. („ „ „ „).
„ Scarlet B.

With other colours the shades obtained are comparable with those produced by recipes (I), (I*a*), and (I*b*) (page 376).

(B.) Indanthrene Colours in "Powder Fine."

Standard Printing Colour.

25–60 grms. Indanthrene dyestuff in "powder fine" are stirred into:
600–800 grms. Standard thickening (*a*), (*b*), or (*c*).
375–140 „ water (or starch-tragacanth paste).

1000

Standard Thickening.

	(*a*.)	(*b*.)	(*c*.)
Starch-tragacanth paste	550	550	520
Glycerine	100	50	100
Glyecine A.	..	50	..
Dissolving Salt B.	..	..	30
Potassium carbonate	150	150	150
Rongalite C. or Formosul	100	100	100
Water	100	100	100
	1000	1000	1000

Reducing pastes as for recipes (I), (I*a*), and (I*b*) (page 376).

The powder brands of Indanthrene colours come into the market in two qualities, viz. (1) powders "fine for printing," and (2) ordinary powders, which may be printed, but are usually recommended for dyeing. As compared with *ordinary paste* brands, as standard, both qualities of powders vary considerably in relative concentration, the powders "fine for printing" being from 3 to 6 times stronger than the corresponding standard pastes, whilst the ordinary powders are 2 to 8 times stronger than the same pastes. The ordinary powders are coarser in texture than the fine printing brands and are only used for printing purposes in countries where tariff charges are levied on bulk weight irrespective of concentration.

The range of powders "fine for printing" at present comprises the following colours :—

Indanthrene Yellow G.*
„ Golden Yellow R.K.
„ Brilliant Oranges G.K. and R.K.
„ Brilliant Pink R.
„ „ Violet R.R.*
„ „ Blue R.*
„ „ Blue 3 G.*
„ „ Green B.
„ „ „ F.F.B.
„ Navy Blue G* and R.R.D.E.*

Indanthrene printing Yellow G.O.K.
„ „ Orange G.O.*
„ „ Red 3 B.
„ „ Magenta B.
„ „ Violet R.F.
„ „ „ B.F.
„ „ „ B.B.F.
„ „ „ F. 4 R.*
„ Red F.B.B.*
„ Rubine R.

The colours marked * in this list are first made into a paste with an equal amount or double the quantity of water; the requisite amount of Glyecine A. is then added and, after standing for a short time, the whole is mixed with the required quantity of standard thickening ((*a*) above).

(C.) Ordinary Powder Brands of Indanthrenes.

These ordinary brands of Indanthrene dyestuffs may, in an emergency, be printed satisfactorily if they are carefully prepared by one of the pre-reduction methods. A typical procedure is as follows:—

Standard Colours.

Recipe.	II.	II*a*.
Indanthrene dyestuff in ordinary powder	20–60	20–60
Nekal B.X. (0·2 per cent. solution) .	20–20	20–20
Water	265–195	245–175
Mix to a paste and add:		
Glycerine	80–100	80–100
Starch-British gum paste . . .	500–400	500–400
Potassium carbonate	80–120	..
Caustic soda 70° Tw..	..	40–80
Hydrosulphite conc. powder ($Na_2S_2O_4$).	15–30	15–30
Heat to 130°–140° F. until reduced completely, cool to 100° F., and add:		
Rongalite C. or Formosul . . .	20–75	50–75
Sodium bicarbonate	..	30–60
Grammes .	1000	1000

Reducing pastes as for recipes (I) and (I*a*). If desired, methylated spirit may be used in place of Nekal B.X. for wetting-out. Glyecine A. and Dissolving Salt B. are added to the above in cases where they are beneficial.

(D.) "Suprafix" Dyestuffs (Indanthrenes, Etc.).

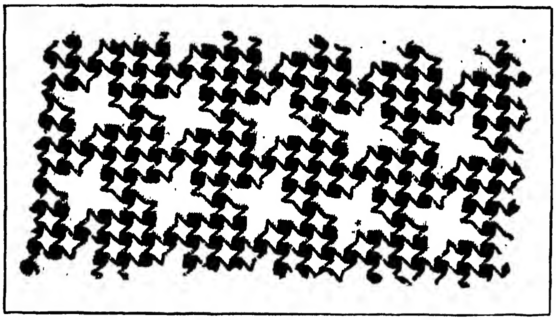
The "Suprafix" dyestuffs represent a new and very interesting addition to the range of Anthraquinone colours available for printing. The group comprises a number of valuable Indanthrene and Algole dyestuffs which, in spite of many attempts, had never been successfully employed in textile printing until, within the last few years, the I. G. Farbenindustrie succeeded in converting them into a special form—a form in which they are now, perhaps, even better adapted to printing purposes than are the ordinary vat printing colours.

The "Suprafix" colours are much less susceptible than other vat colours to irregularities in ageing conditions. They are completely fixed after a short steaming of three minutes in a rapid hydrosulphite ager; and even in cases where the time, temperature, and moisture conditions of the steaming operation are apt to vary between relatively wide limits, they yield consistent results.

The "Suprafix" colours are available only in a paste form which, although of a comparatively liquid consistency, has little tendency to settle out. Neither does it dry up, the paste always remaining in a soft state, being easily stirred if any little deposit has settled out, thus avoiding the irregularities that so frequently occur due to ordinary pastes, which have been stored for some time, settling out and depositing a clay-like mass at the bottom of the cask—a mass that is by no means easy to re-incorporate with the liquid portion of the paste.

Another advantage, of no little importance, is that the "Suprafix" colour pastes are not susceptible to frost.

So far the "Suprafix" colours have not been used to any great extent in textile printing, but once their merits are more widely recognised, they will doubtless displace many of the older vat printing colours. They are as bright and fast as the latter, and the very fact that they are fixed so easily and completely, under various conditions of steaming, ought to commend them to the favourable consideration of calico printers. Practically no difference is to be detected between a print that has been steamed for three minutes in a rapid ager and one that has been steamed for seven minutes in one of the larger modern combined steaming and ageing machines.



Indanthrene Printing Yellow 5 G.K. "Suprafix" (I.G.) (250 grms.: recipe (III*a*)).
,, ,, Black T.L. ,, ,, (250 grms.: recipe (III)).

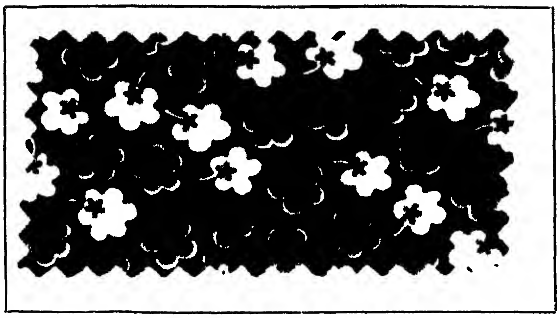
The "Suprafix" dyestuffs are printed by the potash-Rongalite process without previous reduction and without Dissolving Salt B. or other assistants.

Standard Colours.

Recipe.	III.	III*a*.
	grms.	grms.
Indanthrene dyestuff "Suprafix" or "Suprafix" double	100–300	250
Glycerine	80–30	80
Starch-tragacanth paste	500–400	450
Potassium carbonate	80–120	120
Rongalite C. or Formosul	60–100	80
Water	180–50	20
	1000	1000

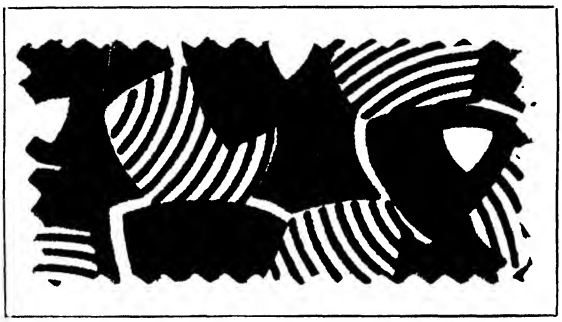
Reducing Pastes.

Recipe.	III.	III*a*.
	grms.	grms.
Crystal gum (1 : 2) or British gum solution	650	650
Glycerine	50	50
Potassium carbonate	50	30
Rongalite C.	40	25
Water	210	245
	1000	1000



Algole Scarlet G.G.N. "Suprafix" (200 grms. (III) (I.G.)).
Indanthrene Brown R.R.D. "Suprafix" (150 grms. (III) (I.G.)).

Printing colours prepared with " Suprafix " dyestuffs can, as a rule, be printed immediately after they have been made-up as above. They reduce quickly and smoothly and are fixed readily and completely, even under conditions of steaming unfavourable to other vat dyestuffs, and they yield very full prints.



Indanthrene Printing Blue G.G. "Suprafix" (60 grms. (III) (I.G.)).
Indanthrene Printing Brown T.M. "Suprafix" (150 grms. (III) (I.G.)).

It should be noted that the " Suprafix " dyestuffs generally require a smaller addition of glycerine than the ordinary paste brands. As the glycerine content varies somewhat according to the conditions under which the printed goods are steamed, it is advisable to ascertain the requisite quantity by a preliminary trial.

The **Cibanone colours**, as previously mentioned, are anthraquinone derivatives similar in general properties and in modes of application to Indanthrene and Caledon dyestuffs. With the exception of Cibanone blue 3 G. and Cibanone yellow G.N., and perhaps one or two others occasionally, they have found but little employment in printing although they are used extensively for dyeing. They may be printed by any of the methods in use for Indanthrenes, but usually they are made-up specially, and yield their fullest shades only in strongly alkaline media. The following examples are typical of the formulæ generally employed :—

Cibanone Brown.

300 grms. Cibanone B. or V. paste (S.C.I.B.).
200 ,, British gum.
50 ,, glycerine.
50 ,, glucose syrup.
50 ,, caustic soda 66° Tw.

Heat to 140° F. till the gum is dissolved, cool, and add—

50 grms. Rongalite or Formosul.
300 ,, caustic soda 66° Tw.

1000

Cibanone Yellow G.N.

100 grms. Cibanone yellow G.N. paste for printing.
600 ,, alkaline thickening C.
100 ,, glycerine.
30 ,, hydrosulphite powder ($Na_2S_2O_4$).
50 ,, water.

Heat to 130°–140° F. for ¼ hour, cool, and add—

40 grms. Rongalite or Formosul.
80 ,, British gum 1 : 1.

1000

Alkaline Thickening C.

1000 grms. British gum.
9000 ,, caustic soda 77° Tw.

Mix, warm gently, and cool.

Cibanone blue 3 G., as illustrated on page 379, may be more conveniently and quite as advantageously printed by the *potash-Rongalite* or *bicarbonate* method described under Indanthrene dyestuffs.

The **Algole colours** and the **Alizarin-Indigos** resemble very closely, in their general properties, the rest of the Anthraquinone series. The Alizarin-Indigos—a group of blue, grey, and brown colouring matters possessing a structure intermediate between the Anthraquinone and Indigoid groups—have now been renamed and such of them as are still made are included in the Indanthrene or Algole groups, according to their fastness properties.

The Algole colours, as a class, are, perhaps, a little brighter than the Indanthrene type, but in all-round fastness they fall below the standard of the latter and, for this reason, they have been grouped apart from the general body of Anthraquinone dyestuffs. In the main, nevertheless, they are of good fastness; the majority of them resist the action of soaping and chlorine satisfactorily, but they leave something to be desired as regards fastness to light.'

The Algole colours come into the market in the form of pastes, powders, and "Suprafix" pastes, all specially prepared, in a fine state of division, for printing. They are applied by the ordinary potash-Rongalite methods (Recipes (I), (I*a*), (I*b*), page 376), and therefore require no further description.

After-treatment of Goods Printed with Indanthrene, Caledon, Algole, and Cibanone Colours.—After the plain bleached goods have been printed, they are carefully dried (see Note (1), p. 385), and then put through the following sequence of operations:—

(1) Aged for 4–5 minutes in a hydrosulphite ager in air-free steam at 214°–218° F. dry-bulb, 212°–216° F. wet-bulb thermometers.
(2) Chromed cold at full-open width in a tank with squeezing rollers at exit; ½–¾ minute passage.
(3) Washed (one beck) in rope form.
(4) Soaped (three becks) in rope form at 180°–212° F.
(5) Washed in square-beater machine; squeezed and plaited down.
(6) Hydro-extracted and finally dried over cans.

Operations (2), (3), (4), and (5) are carried out in a continuous manner and together occupy 15–20 minutes.

The chroming tank (Operation (2) above) is charged with a solution made-up as under:—

CHROME LIQUOR.

50 kilos. bichromate of soda.
30 ,, ammonium sulphate.
20 ,, sulphuric acid 148° Tw.
4000 litres water.

Use cold.

FEED LIQUOR.

12 grms. bichromate of soda.
8 ,, ammonium sulphate.
1000 c.c. water.

During the passage of the printed cloth through the chroming tank, additions of feed liquor are made from time to time, the quantity depending upon the weight of cloth and style of pattern passing through. An average quantity is 4 litres per lump of cloth (120 yards), but very light patterns require less—say one litre feed liquor diluted with 3 litres water, since light patterns consume a smaller proportion of bichromate of soda.

If the chrome liquor begins to evolve ammonia, it must be corrected by an addition of sulphuric acid. Evolution of ammonia indicates that the bichromate of soda has become converted to the neutral chromate and that the bath has diminished in efficiency and requires adjustment. It is advisable to test samples of the liquor three or four times a day when the tank is in continuous operation.

Notes on the Foregoing.—(1) The drying after printing is preferably carried out in a hot air drying apparatus, attached to the printing machine, at a temperature not exceeding 140°–150° F.; and the pieces must not remain in the drying chamber longer than necessary. Prolonged exposure to hot air is liable to cause oxidation of the Rongalite or other sulphoxylate reducing agent and thus result in the production of weak and uneven colours.

(2) It is very important to steam the goods as soon as possible after drying, and equally important to proceed without undue delay to the finishing-off processes of re-oxidation, *e.g.* chroming and soaping at the boil. If the goods are allowed to lie exposed to the air for any length of time either *before* or *after* steaming the colours almost invariably develop unevenly and come up both weak and irregular in shade. If, for any reason, the goods cannot be steamed immediately after printing and drying, they must be wrapped up in cotton wrappers and protected from currents of air, moisture, and especially acid vapours.

(3) Exposure to direct sunlight must be avoided at every stage between the printing and final fixing and soaping of all vat dyestuffs. Even during

re-oxidation, when the goods are saturated with bichromate of soda, an exposure to direct sunlight has been known to destroy beyond redemption so fast a colour as Indanthrene blue G.C.D.

(4) The Indanthrene blues G.C.D., B.C.D., 3 G., R.S., Indanthrene printing blue F.R.S., and Indanthrene brilliant blues 3 G. and R. are all adversely affected, and alter in shade, by too energetic a re-oxidation. If "chromed," the bichromate of soda solution ought to be as weak as possible and used cold, as already recommended (see After-treatment of Indanthrenes, etc.), otherwise over-oxidation, and consequent impoverishment of the colours will occur. In these cases it is best to oxidise with perborate of soda or with hydrogen peroxide and acetic acid:—

$$\left\{\begin{array}{l}\text{2 grms. sodium perborate,}\\ \text{1000 c.c. water,}\end{array}\right\}\text{ or }\left\{\begin{array}{lll}\text{2–3 c.c.} & \text{hydrogen peroxide 30 per cent.}\\ \text{5 ,,} & \text{acetic acid 30 per cent.}\\ \text{1000 ,,} & \text{water.}\end{array}\right.$$

Both used at 110°–130° F.

These peroxides have no effect on the shade of the above blues. They may also be used, if desired, for the re-oxidation of any vat dyestuff, in place of bichromate of soda.

(5) Vat colour prints on goods prepared with β-naphthol and Naphthol A.S. brands generally come up fuller. Additions of phenolates and naphtholates to the printing colours also produce, in many cases, the same effect.

(6) The reduction, solution, and fixation of a number of Indanthrene (and similar) dyestuffs are facilitated by additions of Glyecine A. or Dissolving Salt B.

Additions of Glyecine A. improve the quality and yield of the following colours:—

Indanthrene Rubine R.
,, Brilliant Violet R.R.
,, Printing Violets B.B.F., F. 4 R., and F. 3 B.
,, Navy Blues G., R., and R.R.D.E.
,, Dark Blue B.O.A.
,, Brilliant Blues R. and 3 G.
,, Blues R.S., G.C.D., B.C.D., and 3 G.
,, Blue Green F.F.B.
,, Brilliant Greens B., G.G., F.F.B.
,, Greys M. and 3 B.
,, Printing Black B.R.

Dissolving Salt B. exerts a similar favourable influence on—

Indanthrene Brilliant Pink B.
,, Rubine R.
,, Violet F.F.B.N.
,, Navy Blues G. and R.
,, Dark Blue B.O.A.
,, Blue Green F.F.B.
,, Red Brown R.
,, Grey M.
,, Olive 3 G.
,, Printing Black B.R.

The "Suprafix" dyestuffs, which possess excellent fixing properties, require no additions of any description; in fact such additions are, for the most part, detrimental.

(7) If, for some reason or other, it be thought desirable to work a strongly caustic colour in combination with potash-Rongalite colours, it is well to note that, in practice, such colours do not work well together. If the caustic colour works before the carbonate colours in the printing machine, the following carbonate roller picks up caustic soda from the printed cloth; if, on the contrary, the carbonate colours work first, carbonate of potash is similarly transferred to the caustic roller. In either case carbonate of potash is salted out or precipitated in granular form on the unengraved surface of the rollers, and in this state it scratches and etches them, with the result that they print portions of the cloth for which they were not intended. Again, if the carbonate colour contains much glycerine, the etching proceeds at a greater rate, for it is a well-established, though little known, fact that the combined action of caustic soda and glycerine on bright copper causes a pitting of its surface. It is probable, too, that sodium and potassium carbonates along with glycerine produce the same effect to a less degree, and this may be the explanation of the smearing or "scum" that frequently appears on the white grounds of goods printed with vat colours.

(8) Owing to the growing demand for all-round fastness in printed goods, the Anthraquinone dyestuffs are coming more and more into general use for the printing of natural and artificial fabrics, in styles that were previously executed by means of Alizarin, Chrome, and Basic colours.

The following list, selected from the extensive range now available, indicates some of the best and most popular colours employed in the production of the highest class of fast work in this country:—

Indanthrene	Printing Yellow 5 G.K. "Suprafix"	(I.G.)
,,	Yellow 3 G. "Suprafix"	(,,)
,,	Golden Yellow R.K. "Suprafix"	(,,)
,,	Printing Yellow G.O.K. paste	(,,)
,,	Golden Orange 3 G. paste	(,,)
,,	Brilliant Orange G.K. paste	(,,)
,,	,, ,, G.R. "Suprafix"	(,,)
,,	,, ,, R.K. "Suprafix"	(,,)
,,	Scarlet R. paste	(,,)
,,	,, B. paste	(,,)
,,	Printing Red B. paste	(,,)
,,	,, ,, F.F.B. powder fine	(,,)
,,	,, Pink F.F.B. paste	(,,)
,,	,, Magenta B. "Suprafix"	(,,)
,,	,, Violet R.F. and B.F. pastes	(,,)
,,	,, Blue R. paste	(,,)
,,	,, ,, B. "Suprafix"	(,,)
,,	,, ,, F.R.S. paste	(,,)
,,	,, ,, G.C.D. and B.C.D. pastes	(,,)
,,	Blue Green F.F.B. double paste	(,,)
,,	Brilliant Green B., F.F.B., G.G., and 4 G. pastes conc.	(,,)
,,	Red Brown R.R.D. "Suprafix"	(,,)
,,	Printing Brown R.S. paste	(,,)
,,	Grey 3 B. and M. pastes	(,,)
,,	Printing Blacks B., B.L., and T.L. "Suprafix"	(,,)

Caledon Yellow G. 200 paste	(I.C.I.)
,, ,, R. 250 paste	(,,)
,, Orange 4 R.S. and 2 R.T.S. pastes	(,,)
,, Gold Orange G. and 3 G.S. pastes	(,,)
,, Brilliant Orange 4 R.S. paste	(,,)
,, Red B.N.S. and 2 G.S. pastes	(,,)
,, Brilliant Purple 2 R. and 4 R.S. pastes	(,,)
,, Jade Green X. 200 paste	(,,)
,, ,, ,, B. 200 paste	(,,)
,, ,, ,, G.S. paste	(,,)
,, Brown R.S., G.S., 2 G. and 5 G. pastes	(,,)
,, Yellow Brown 3 G. paste	(,,)
,, Blue G.C.P.S. and R.S. pastes	(,,)
,, ,, 3 G.S. paste	(,,)
,, Brilliant Blue 3 G.S. and R.S. pastes	(,,)
,, Dark Blue B.M. 200 paste	(,,)
,, ,, ,, R.R.D.S. paste	(,,)
,, Printing Black B.R. 200 paste	(,,)
Durindone Brown 4 B.S. and G.S. pastes	(,,)
,, Pink F.F.S. and F.B.S. pastes	(,,)

Cibanone Blue 3 G. paste	(S.C.I.B.)
,, ,, 3 G.F. paste	,,
,, Yellow G.N. paste	,,

Of the foregoing colours the Indanthrenes come into the market as single pastes, double pastes, and powders, all marked " fine "—also as " Suprafix " brands where so indicated. The Caledon and Cibanone colours in printing qualities are available only in paste and double pastes. As a rule pastes are easier and more convenient to deal with than powders however fine, but, with the exception of the " Suprafix " pastes, they are apt to dry up, settle, and sometimes freeze ; hence they demand care in storage.

The Sulphurised Vat Colours.

The Hydron and Alizanthrene blues and the Hydron and Indocarbon blacks are, at present, the only members of this group of dyestuffs. In their mode of formation and in many properties the Sulphurised vat colours resemble ordinary Sulphur colours, but differ from them in being much more highly sulphurised. According to Wahl and Atack they are prepared by the intensive sulphurisation of Indophenol-carbazol, its substitution products, alkyl or acyl derivatives, or of certain of its condensation products ; all of which operations lead to the production of very fast vat dyes which come into the market under the names of Alizanthrene navy blue, Hydron blues G. and R., Hydron printing blues, Hydron and Indocarbon blacks. Hydron violets consist of mixtures of Hydron blue and Thioindigo red 3 B. and, therefore, do not belong rightly to the group. The rest of the so-called Hydron colours, viz. reds, pinks, scarlets, oranges, etc., are similar in character to the Indigoid dyestuffs. They yield the same shades, they possess much the same properties, and they are applied by exactly the same methods as corresponding colours in the Indigoid series. Possibly they differ to a slight extent from their prototypes in this series, and in individual cases they may represent perhaps an improvement upon them, but for all practical purposes they are the same and call for no special description. Hydron yellow also is not a

true sulphur vat dyestuff, though it is derived from the same base as Hydron blue, viz. carbazol.

A desire has long existed among calico printers for a colour which, while possessing the depth and fastness of Indigo, would be capable of being applied in such a way as to obviate the disadvantages entailed by the necessity for printing Indigo in a strongly alkaline medium. The Hydron blues more than fulfil these conditions, for they are faster even than Indigo, and are applied with *weak* alkalies, such as the carbonates of soda and potash.

Hydron blue R. gives deep full shades of Indigo; Hydron blue G. yields lighter and greener shades, rather brighter than light Indigo; and Hydron printing blue 3 R. a very dark colour, chiefly used for shading purposes. All three brands are not only fast to soaping, acids, and alkalies, but also to light and chemicking, which cannot be said of even medium, not to speak of pale, shades of Indigo.

Hydron blues (I.G.), whether printed or dyed, may be resisted by the usual resists (zinc and copper salts, Leucotropes, etc.) used for other vat colours, but once dyed they cannot be discharged by any known process; hence their application is, at present, restricted to direct printed, cover and pad, and "dipped" styles, so that Indigo still holds its own for discharged styles.

The Hydron blues may be mixed with other vat colours for the production of compound shades, worked along with them in multicoloured patterns, and generally applied to the same purposes, their mode of application being practically identical.

Hydron blue R. may, if desired, be printed by any of the methods employed for Indigo, but Hydron blue G. is best suited to the sulphoxylate-carbonate process, which, in fact, yields the most satisfactory results with both colours.

The following recipe is recommended for the preparation of the printing colours:—

50	grms.	Hydron blue R. or G. or Alizanthrene navy blue (40 per cent. pastes).
40	,,	glycerine.
200	,,	water.
50	,,	potassium carbonate.
60	,,	glucose.
50	,,	Dissolving Salt B. (benzyl-sulphanilate of soda).
50	,,	sulphoxylate-formaldehyde 50 per cent. solution.

Heat to 140° F. for $\frac{1}{4}$ hour, cool a little, and add—

500	grms.	thickening H.
1000		

Lighter shades are obtained by adding more thickening.

THICKENING H.

150	grms.	wheat starch.
550	,,	water.
300	,,	gum tragacanth 6 per cent.
1000		

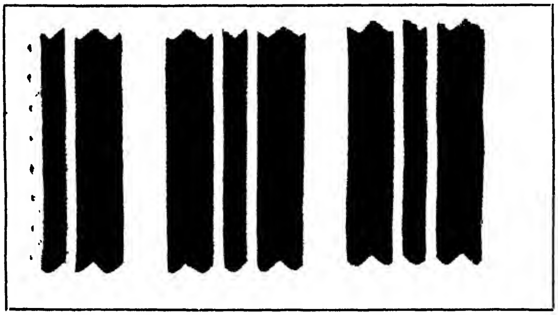
Print, dry, and steam for 4–5 minutes at 104° C. in steam as free from air as possible; then sour slightly with the addition of a little bichromate of soda (5 grms. sulphuric acid and $2\frac{1}{2}$ grms. bichromate per litre), wash well, soap, wash, and dry. Alizanthrene navy blue, made by the British Alizarine Co., is identical with Hydron blue R.

Brighter results are obtained with Hydron blue G. by replacing the souring by a treatment in perborate of soda ($1\frac{1}{2}$ grms. per litre) at 105°-120° F.

The *bicarbonate process* of printing vat colours is also well adapted to the Hydron colours, and gives excellent results in practice.

Among the later additions to the Hydron group of colours, derived from carbazol, three of great technical importance—Hydron printing blue 3 R., Indocarbon C.L., and Hydron black C. "Suprafix"—deserve special consideration.

Hydron Blue 3 R. (in paste) is a new vat dyestuff of great tinctorial strength which, when printed by the potash-Rongalite method with a relatively small quantity of potash and without Dissolving Salt B., fixes with remarkable ease on vegetable and animal fibres and yields bright navy blues of a reddish tone. The prints obtained, though not of Indanthrene fastness, are yet very fast, withstanding well the action of chlorine, light, and boiling soap.



Hydron Printing Blue 3 R. (I.G.).

The pattern illustrated has been produced by the following process:—

DARK BLUE.

150	grms.	Hydron printing blue 3 R. paste.
30	,,	glycerine.
30	,,	Glyecine A.
150	,,	water.
500	,,	starch-tragacanth paste.
70	,,	potassium carbonate.
70	,,	Rongalite C.
1000		

LIGHT BLUE.

Dark blue reduced 1 : 3.

REDUCING PASTE FOR LIGHT SHADES.

650	grms.	British gum thickening (1 : 1).
20	,,	glycerine.
20	,,	Glyecine A.
250	,,	water.
30	,,	potassium carbonate.
30	,,	Rongalite C.
1000		

Print, dry, steam in the hydrosulphite ager with moist air-free steam at 214° F., chrome, wash, and soap as usual for vat colours.

Hydron printing blue 3 R. resists perfectly the action of excess of sulphoxylate-formaldehyde (Rongalite, Formosul, etc.), and may be used for the

production of fine, bright, dark blue discharges on nearly all fibres dyed with dischargeable acid, direct, Naphthol A.S., and vat dyes.

Indocarbon C.L., on its introduction a few years ago, marked the appearance of the first really satisfactory vat colour printing black. Up to that time none of the vat blacks available had ever been used to any considerable extent for printing purposes. As a class they were unwillingly avoided, in practice, as much as possible. If they were not prohibitive in price (cost of production) they were either not fast enough, or they yielded colours which could only be dubbed " black " by courtesy; hence they were replaced in fast colour work by Aniline or Sulphur blacks which, whilst not fast to chlorine, did at least give full rich blacks at an economic price—blacks which were of excellent fastness to light and boiling soap.

Indocarbon C.L., unfortunately, is not an easy colour to print if the printing colour is made up directly from the ordinary dry powdered colouring matter as marketed. In this state it contains too high a percentage of extraneous matter (used for standardising purposes) to allow of a good printing colour being prepared from it, and it yields poor prints. But if suitably treated, and worked according to the second of the processes to be described, it not only prints well but also gives deep blacks which are fast to light, soaping, and chlorine.

An improved quality of the above dyestuff is represented by Indocarbon C.L. *concentrated*—a finely divided powder specially prepared for printing. It certainly works more easily than the original brand as such, but the latter, when purified by washing, is by far the better of the two for printing purposes, both as regards yield and cost.

Indocarbon C.L. reduces easily with hydrosulphites and potassium or sodium carbonate, but, curiously enough, it cannot be fixed satisfactorily in steaming when printed by the ordinary potash-Rongalite process. The best results are obtained, and are only obtainable, when the colouring matter is reduced, before printing, with glucose and caustic soda, with or without a subsequent addition of Rongalite or Formosul. In most cases, too, it is preferable to employ the *ordinary* powder quality in the form of a purified paste containing 40–50 per cent. of dyestuff. Indocarbon C.L. *concentrated powder* may be used successfully, but it is more expensive and yields no better results.

The following recipe for the preparation of a printing colour is based upon the formula recommended by the makers of Indocarbon C.L. (I. G. Farbenindustrie A.G.):—

INDOCARBON C.L. (A).

140	c.c.	water.
86	,,	caustic soda 64° Tw.
30	grms.	soda-ash.
120	,,	Indocarbon C.L. (40 per cent., see page 392).
60	,,	glycerine.
100	,,	glucose syrup.
450	,,	British gum-starch paste.

Mix, heat at 140°–160° F. until reduced, and then add—

20 grms. Rongalite C. (ground).

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This recipe is suitable only for the printing of fairly heavy patterns; it is too weak in colouring matter for fine line or cover work.

A much better recipe, which has given excellent and consistent results in practice and is suitable for all classes of work from the finest shirting styles to the heavier patterns used in garment printing, is the following :—

INDOCARBON C.L. (B): STANDARD COLOUR.

240 grms. Indocarbon C.L. (40 per cent. paste).
125 c.c. caustic soda 64° Tw.
95 grms. glucose syrup.
400 ,, thick gum arabic mucilage (neutral).

Heat to 120° F. for ½ hour, cool, and add—

55 grms. sodium bicarbonate.
60 c.c. water.
5 grms. potassium cyanide (KCN).
20 c.c. water.

Bulk to 1000 c.c.

For reducing the strength of the black, add the necessary quantity of the following thickening :—

REDUCTION THICKENING.

100	grms.	glycerine.
550	,,	thick gum arabic mucilage.
50	,,	potassium carbonate.
50	,,	soda-ash.
250	,,	water.
1000		

The full-strength standard colour is used only for the finest line prints and light, delicately engraved patterns. For general printing 3 : 1 reduction is usually as strong as is necessary, while for heavy objects and strong engraving a 2 : 1, or even a 1 : 1, reduction is often not too weak in colour to produce a good black.

3 : 1 INDOCARBON BLACK.

3—Standard colour (B).
1—Reduction thickening (above).

The *purification of Indocarbon C.L.* is effected by the simple process of washing and filtering. About 20 kilos. of dyestuff are washed twice, by decantation, with boiling water—100 litres or more being used each time. The dyestuff is then allowed to settle, and the bulk of the supernatant liquor syphoned off and the precipitate thrown on a cloth filter and allowed to drain until it contains 40 per cent. total solids.

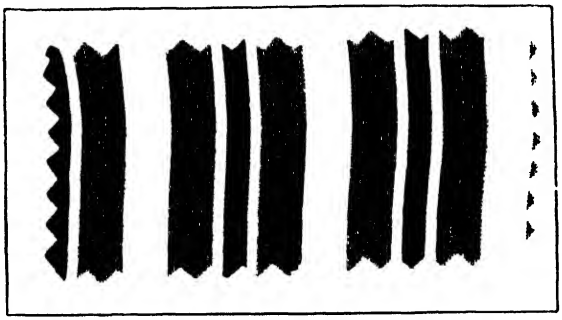
After printing, the goods are steamed for 4–5 minutes in air-free steam and then chromed, washed, and soaped at the boil according to the usual procedure for vat colour prints.

Hydron Black C. " Suprafix."—From its name, its brand mark, its mode of application, its derivation from carbazol and its general properties, Hydron Black C. " Suprafix " may be assumed to be a refined form of Indocarbon C.L. or an analogous body. Like other " Suprafix " dyestuffs it is marketed as a thin paste which is frost-proof and has little or no tendency to settle out. Printed by the special method described below, with Rongalite, soda-ash, and glucose, it works well and is very easily fixed on the fibre even under varying

steaming conditions. On cotton and artificial silk fabrics and mixtures of these it yields full deep blacks of excellent all-round fastness ; the black prints may be classed as of Indanthrene fastness, but the greys, obtained by reducing the strength of the black printing colour, are not up to that standard, being looser to chlorine and also somewhat looser to light and soaping.

HYDRON BLACK C. " SUPRAFIX " (PRINTING COLOUR).

180	grms.	Hydron black C. " Suprafix."
70	,,	cold water.
750	,,	stock thickening (below).
1000		



Black: Hydron Black C. "Suprafix" (180 grms. per kilo.) (I.G.).
Grey: " " " 1 : 4 (36 grms. per kilo.) (I.G.).

STOCK THICKENING.

550	grms.	starch-tragacanth paste.
40	,,	glycerine.
40	,,	Glyecine A.
65	,,	soda-ash.
200	,,	glucose 1 : 1.
40	,,	Rongalite C. (Formosul, etc.).
65	,,	water.
1000		

Heat gently and cool before use.

THICKENING FOR REDUCTIONS.

600	grms.	crystal gum or British gum thickening.
20	,,	glycerine.
20	,,	Glyecine A.
20	,,	soda-ash.
80	,,	glucose 1 : 1.
20	,,	Rongalite C.
240	,,	water.
1000		

After printing, the goods are dried, steamed for 3–5 minutes in the hydrosulphite ager with air-free steam at 214° F., and then chromed, washed, and soaped as usual.

Hydron Black C. "Suprafix" is much more convenient and more easily fixed than Indocarbon C.L., but the latter is cheaper and, in spite of the extra work entailed by its purification, is still preferred in works where the initial difficulties of its application have been overcome. Moreover, it yields a black which leaves little to be desired in the way of depth and fastness.

The Colloresine Process of Printing Vat Dyestuffs.

In this process, introduced by the I. G. Farbenindustrie A.G. in 1928, advantage is taken of the characteristic property possessed by the thickening agent Colloresine of being precipitated from its aqueous solutions by heat, or by the addition of neutral salts or alkalies, and of re-dissolving when the solution is cooled or when the precipitate is washed free of the additions with cold water. The practical value of this property is that printing colours thickened with Colloresine neither "mark-off" nor "bleed" when the printed goods, subsequently, are padded through hot alkaline solutions of a reducing agent, and steamed in the wet state, for the purpose of developing and fixing the printed colours. The temperature at which these operations are conducted is sufficiently high to coagulate the Colloresine which, in such condition, encloses the colouring matter in an insoluble envelope and thus prevents it from spreading beyond the limits of the printed pattern, holding it firmly in place until it is fully developed and fixed. The Colloresine is then removed from the printed cloth by a thorough wash in *cold* water, in which it re-dissolves readily, leaving the goods in a soft state suitable for any type of finish.

The Colloresine-hydrosulphite process is carried out in two major stages, viz. (*a*) the printing, and (*b*) the developing and fixing processes. The printing colours contain neither alkali nor reducing agent, consisting solely of dyestuff, thickening matter, and such assistants as exercise a beneficial effect at later stages, and consequently the printed goods may be dried at any temperature and allowed to lie exposed to the air without detriment for any length of time before proceeding to the final stage of the process—development and fixation. When convenient, the printed goods are passed through a hot developing bath, steamed without drying for about half a minute, re-oxidised, and washed off in cold water, the whole series of operations being carried out in a continuous manner.

The unrestricted interval between the printing and the development of the colours, and the elimination of the rapid hydrosulphite ager for developing and fixing purposes, are two features of the Colloresine process which constitute advantages of great importance to block printers and others engaged in decorating textiles by methods of stencilling and spraying, and of real value also for roller printing in bulk. The practical advantage, of course, lies in the fact that any number of pieces may be printed without taking into consideration the necessity, demanded by other processes, for steaming and finishing off the printed goods immediately, or as soon as possible, after printing. The undeveloped, unsteamed goods printed by the Colloresine process undergo no change in storage and may be kept without fear of injury until such time as is convenient for their final treatment.

In preparing printing colours with Colloresine it is usual to employ a mixture of Colloresine and starch thickenings. Colloresine alone yields colours which are both weaker in shade and less fast to washing than those obtained by admixture with starch paste. The amount of starch thickening to be added must not exceed 60 per cent. at the outside, and this quantity only when the dyestuff to be printed is difficult to reduce to its leuco compound; a larger percentage of starch reduces the protective action of Colloresine to a point at

which it fails to prevent "marking-off" and "bleeding" during the processes of development and steaming. For most purposes, not more than 50 per cent. of starch thickening (calculated on the total weight of thickening) ought to be employed if sharp prints and uniform work are desired. The colouring matters most suitable for printing by the Colloresine process are, with some exceptions, identical with those used for ordinary vat colour printing, preference being given to those "paste fine" and "powder fine for printing" brands which have been expressly prepared, in an extremely fine state of division, for printing purposes.

The preparation of the printing pastes is a very simple business. The colouring matter is merely made into a smooth, creamy paste with cold water, then stirred into the starch thickening, and when thoroughly incorporated the whole is finally added to the Colloresine thickening. Any additions, such as Dissolving Salt B. or Glyecine A., are best added before mixing with the Colloresine.

The *modus operandi* of the Colloresine-hydrosulphite process of printing vat colours is as follows:—

PRINTING COLOUR.

50–200	grms.	Vat dyestuff in paste.
335–185	,,	water.
300–300	,,	starch paste 10 per cent.
300–300	,,	Colloresine thickening D.K.
15–15	,,	castor oil (or Depanol J.).
1000		

THICKENING FOR REDUCTIONS.

300	grms.	starch paste 10 per cent.
50	,,	Glyecine A.
300	,,	Colloresine thickening.
350	,,	water.
1000		

COLLORESINE THICKENING D.K.

940 grms. water at 175° F. are poured over
40 ,, Colloresine D.K.

Allow to swell and soften, stir well, and add—
20 grms. ammonium sulphocyanide.

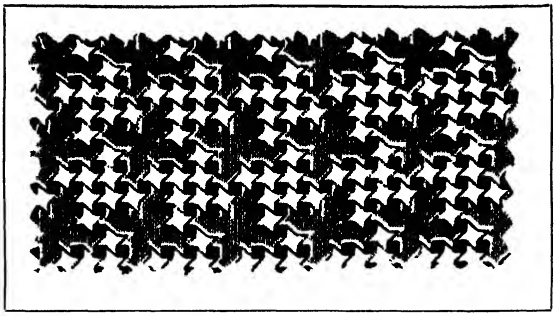
1000

On cooling to about 80° F. the Colloresine goes into perfect solution.

STARCH PASTE 10 PER CENT.

100 grms. wheat starch.
880 ,, water.
20 ,, ammonium sulphocyanide.

Boil and cool.



Orange: Indanthrene Brilliant Orange G.R. "Suprafix" (150 grms. per kilo.) (I.G.).
Violet: Indanthrene Printing Red Violet R.R.N. "Suprafix" (150 grms. per kilo.) (I.G.).

Printed by the Colloresine and developed by the Rongalite process.

Colours prepared according to the foregoing formulæ are printed on plain bleached materials, dried either over steam-heated cylinders or in hot air chambers and, if desired, stored in readiness for fixation at any convenient subsequent period.

The fixation is best effected as follows: The printed goods are first padded in a three-bowl padding mangle through a developing bath consisting of an alkaline solution of sodium hydrosulphite, at a temperature of about 85° F., the pressure of the mangle bowls being adjusted to give an expression of 80–90 per cent., *i.e.* to allow of the cloth carrying forward 80–90 per cent. of its weight of developing liquor. The goods are then steamed at once *in the wet state* for 30 seconds in dry steam at 230°–240° F. in a small jacketed steaming chest situated immediately behind the padding mangle. From the steaming chest the goods pass directly into an open washing and fixing machine in which they are successively washed by spray pipes in the first compartment, soured with weak acetic acid in the second, re-oxidised in the third with a solution of perborate of soda (0·5 gramme per litre) at 120° F. and, finally, washed again in the last compartment with cold water. After this, the goods may be washed in the rope form and soaped as usual to brighten the shades and clear the white ground of the print.

Developing Bath.

200	grms.	common salt.
800	c.c.	water.
2	,,	Monopol brilliant oil (or soluble oil).
20	,,	acetone.
90	,,	caustic soda 76° Tw.

Add immediately before use:—

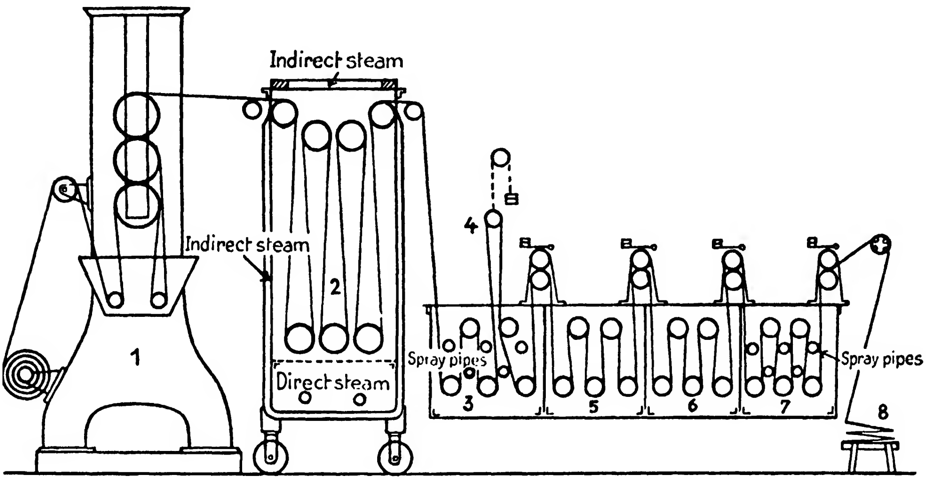
30–40 grms. sodium hydrosulphite conc. powder ($Na_2S_2O_4$) according to the concentration of the printing colour.

Bulk to 1000 c.c.
Use at 85° F.

The developing bath must be replenished at frequent intervals as it is somewhat unstable if used for long.

The type of apparatus employed in carrying out the foregoing series of operations is illustrated in fig. 78.

If, instead of passing the goods from the steamer directly into water, they are first re-oxidised in the bichromate-sulphate of ammonia-sulphuric acid bath used in the ordinary processes of printing vat colours, rather darker colours are obtained. There is always a possibility that a certain amount of colour will be lost in washing if the steamed goods are passed immediately into water; the colours on the cloth are still in the leuco state, to a greater or less extent, and as the whole of the original alkali is also present, the wash water



1. Three-roller padding machine.
2. Steaming chest.
3, 5, 6, 7, 8. Open washer and fixer.
4. Tension adjustor.

FIG. 78.—Developing machine for the Colloresine process.

frequently becomes a dilute dyebath, and not only abstracts colour from the printed pattern but also tints the white unprinted portions of the cloth. The remedy is to wash the cloth with spray pipes, letting the water run away, until all alkali is removed or, as above, to re-oxidise at once immediately after steaming.

In the event of tinted grounds being required, the requisite quantity of a vat dyestuff suitable for padding in a reduced condition may be added to the developing bath; generally, however, such tints are preferably produced at a later stage.

The advantages claimed for the new Colloresine-hydrosulphite process as compared with the usual steaming processes are as follows:—

(1) Perfect stability of the printing colours and of the unsteamed prints.
(2) No injury to the colours by overheating in the drying apparatus of the printing machines.
(3) A saving in steam, labour, and time owing to the elimination of the usual passage through a rapid ager.
(4) The possibility of the simultaneous production of tinted grounds by adding appropriate dyestuffs to the developing bath.
(5) The production of vat colour resists, free from halo, under Aniline blacks.

(6) Increased production from the printing machines and greater certainty in working.
(7) Printed goods may be stored as long as desired without detriment. The omission of the usual ageing process obviates the frequent necessity for working overtime at enhanced rates of pay.

An alternative to the hydrosulphite developing bath is to pad the Colloresine prints through an alkaline solution of Rongalite C., dry in a hot flue, and then steam for 5–10 minutes in the hydrosulphite ager with moist steam at 214° F. Obviously the only advantage of this variation lies in the stability of the unsteamed prints and the production of halo-free vat colour resists under Aniline black. In other respects it is little superior to the usual potash-Rongalite process and its variations.

The process is as under:—

PRINTING COLOUR.

150	grms.	Vat dyestuff in paste.
200	,,	water.
350	,,	starch thickening 10 per cent.
300	,,	Colloresine D.K. thickening.
1000		

Print, dry, and pad through the following:—

DEVELOPING SOLUTION.

100	grms.	Rongalite C.
100	,,	potassium carbonate (or 50 grms. soda-ash).
500	,,	water.
75	,,	glycerine.
3	,,	Nekal B.X. dry.
50	,,	Glauber's salt.

To 1000 grms. with water.

The padding is done in an ordinary 3-bowl mangle with hot flue attached. Dry after padding and, as soon as possible, steam for 5–10 minutes at 214° F. in a rapid ager as already described. Then wash, chrome, and soap as usual.

The production of vat colour resists under Aniline black with Colloresine will be described later in the section dealing with "resists" and "discharges."

Indigosols.

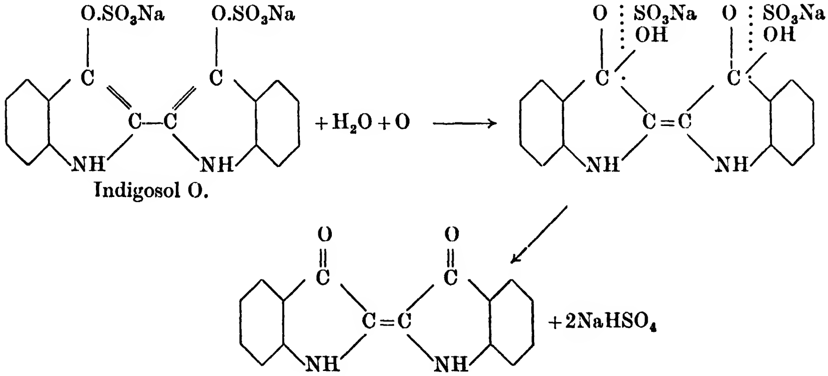
The announcement, in 1881, of Baeyer's solution of the problem of preparing Indigo synthetically, in bulk, followed later by other solutions of the same problem (Baeyer and Drewsen, 1882; Heumann, 1900, etc.), encouraged the hope that these synthetic processes, of which the final phases were capable of being effected on the fibre itself, would provide a simpler and more convenient method of printing Indigo than that afforded by the then newly introduced (1883) Schlieper-Baum glucose process. This classic process, simple enough in theory, and unsurpassed for the beauty and richness of the Indigo prints produced by its means, presents certain difficulties in practice which have prevented its general adoption as a current routine process; it still remains, after over fifty years, a speciality of relatively few firms. It entails the use of strongly alkaline (caustic) printing colours, the inconveniences of which are too generally recognised to need setting out; it is a delicate process—the reactions upon which it is based must be regulated to a nicety, and brought about under certain well-defined conditions of steaming, which admit of little variation if

full, even colours are to be obtained; and finally, the printed goods must be finished off as soon as possible after printing and be carefully protected from undue exposure to currents of air, acid vapours, and damp, and, during printing, from overheating in the drying chambers. The conditions under which the Schlieper-Baum process yields the best results may vary somewhat, between narrow limits, in different printworks, but, once established, the appropriate conditions must be maintained, otherwise a loss of Indigo will occur. The steaming operation is especially important; *under-steaming*, if ever so little, results in the imperfect reduction of the dyestuff and, consequently, its imperfect fixation, whilst *over-steaming* produces over-reduction and a partial destruction of Indigo; time, temperature and humidity of the steam are also factors of importance and call for accurate adjustment according to the plant available. In short, the printing of Indigo by the glucose-alkali (or hydrosulphite-alkali) process is a delicate and difficult style that demands considerable experience and careful supervision for successful production.

Such being the case, it is not surprising that the various syntheses of Indigo excited the keen interest of calico printers, not so much because they foreshadowed the manufacture of synthetic Indigo in substance, but rather because they apparently presented a possibility of producing Indigo directly on the fibre by a simple straightforward process which would supersede the difficult Schlieper-Baum process. Up to a point these hopes were realised but, unfortunately, none of the new synthetic methods could, by any means, be made to yield more than a medium shade of Indigo (and that, more often than not, irregular) and, consequently, they were of little industrial value and quickly fell into almost complete disuse.

The idea of producing Indigo directly on the fibre, on an industrial scale, lay dormant until in 1922 Messrs Durand, Huguenin, of Bâle, revived it suddenly by the introduction of Indigosol O.—an entirely new and stable sulphonated derivative of Indigo.

Indigosol O., a soluble and stable salt of Indigo-white, was discovered by Bader and Sunder in 1920–21,[1] and is prepared by treating leuco-indigotin, in an atmosphere of carbon dioxide, with a pyridine solution of chlorosulphonic acid. From the sodium salt of the resulting enolic ester, which is stable to air, Indigo is regenerated instantaneously and quantitatively by gentle oxidation in acid media—nitrous acid, ferric chloride, sodium chlorate, etc.—according to the following equation:—



Indigosol O.

Indigo.

[1] English patent No. 24602, 1921. (M. Bader and C. Sunder).

Indigosol O. is easily applied to fabrics consisting of vegetable and animal fibres in the form of a neutral or faintly alkaline solution, thickened or not according to whether it is to be printed or padded. The regeneration of the Indigo may be effected either (1) by passing the printed or padded goods through a bath containing the necessary oxidising agents or acid capable of bringing about oxidation, or (2) by a short steaming operation, in which case the printing colour or padding liquor contains, in addition to Indigosol O., suitable oxidising agents and other bodies from which acid is split-off at high temperatures. These two principles underlie all applications of Indigosol O., and also of later analogous colouring matters prepared from substituted Indigos and Anthraquinone dyestuffs. They may be summarised as follows:—

(1) Print a thickened solution of Indigosol O.; dry and pass through a bath of ferric chloride or other suitable oxidising agent; wash, and soap.

(2) Print a mixture of Indigosol O. and sodium nitrite; dry and pass through a dilute solution of sulphuric acid; air a short time, wash, and soap.

(3) Print a mixture of Indigosol O., chlorate of soda, sulphocyanide of ammonia, and vanadate of ammonia; dry, steam 4 minutes, wash, and soap.

Examples of (1) and (2) have already been given on pages 350 and 351; the mixture for a typical example of (3) is made up as under:—

$\left\{\begin{array}{lll} 80 & \text{grms.} & \text{Indigosol O.} \\ 250 & ,, & \text{water (hot).} \end{array}\right.$

Dissolve and add:—

530 grms. starch-tragacanth thickening.
60 ,, sodium chlorate 10 per cent. solution.
30 ,, ammonium sulphocyanide (50 per cent. solution).

Cool completely and add:—

50 grms. ammonium vanadate 1 : 1000.

1000

Print, dry in hot air, steam 4 minutes in a rapid ager, wash and soap if necessary.

By replacing the greater part of the thickening with water this method may be used equally well for the production of plain shades of Indigo by padding. Usually, however, the first two methods are preferred for this purpose, since they not only yield brighter shades, but are also more convenient for certain special resist styles which will be described at a later stage.

It will be noticed that the foregoing steaming process (3) for the formation of Indigo on the fibre is practically identical in principle with the various methods employed for the production of Aniline black. The resemblance is emphasised by the fact that the development of Indigosol O., like that of Aniline black, is prevented by the presence of alkalies, reducing agents, or salts which neutralise the mineral acid content of the printing or padding colours, *e.g.* hydrosulphites, acetates of soda or magnesium, thiosulphate of soda, carbonates of soda or potash, etc. Thus, it is possible to realise, on grounds of veritable Indigo, effects exactly parallel to those obtained on black grounds by means of the well-known Prud'homme Aniline black reserve style—effects hitherto unobtainable with Indigo by any known means. Moreover, during recent years, soluble stable esters of many vat dyestuffs have been prepared, on the lines of Indigosol O., and as they are all applied by similar means, it is now possible to produce a vast variety of reserve and discharge styles in fast colours on fast grounds of almost any conceivable shade—an achievement undreamt of a few years ago.

In spite of the ready adaptability of Indigosol O. to all classes of Indigo

work, its relatively high price has, unfortunately, restricted its use to the production of such special styles as fall outside the scope of ordinary Indigo technique. For direct Indigo prints, and for white reserves under printed pads and covers, the Schlieper-Baum process still reigns supreme, notwithstanding its difficulties ; it is the cheapest process and, in expert hands, it yields a full range of blues which, for purity and evenness in pale shades and for depth and richness in dark ones, leave little to be desired. On the other hand, when it is a question of producing multicolour resists in fast bright colours under Indigo pads and covers or on plain padded grounds, Indigosol O. comes into consideration, since it affords the only practicable means of obtaining such effects on a genuine Indigo background.

From the foregoing discussion it will be recognised that the introduction of Indigosol O., apart from its scientific interest and its solution of a long-standing problem, was an event of great technical importance to calico printers in general. In addition to providing simpler, more convenient, and more expeditious means of executing current Indigo styles, and affording reliable methods of producing novel reserve and discharge effects previously unattainable, it opened up a new field of research and indicated methods of preparing a new series of stable leuco compounds of fast dyestuffs, all constituted on similar lines and applicable by the same general methods.

Since the appearance of Indigosol O., in 1922, the Bader and Sunder process, with some modifications, has been applied to the solubilising of other vat dyestuffs of the Indigoid and Anthraquinone groups. Colouring matters of this type derived from substituted Indigo, Indanthrene, Algole, and Helindone dyestuffs are designated " Indigosols " (Durand, Huguenin : I. G. Farbenindustrie) ; those derived from Caledon dyestuffs are known as " Soledons " (Scottish Dyes, Ltd.). The two classes are closely related to each other in general structure and properties, but are not identical, since the Soledons, unlike the Indigosols, possess an affinity for the cotton fibre, which they dye directly, acting in this respect like ordinary direct dyestuffs. Otherwise the groups behave similarly ; both consist of soluble and stable esters of the leuco bases of vat dyestuffs ; both may be applied in printing and dyeing by similar methods ; and from both the original dyestuff is regenerated by simple oxidation on the fibre.

At the same time, the substantivity of the Soledon colours renders them less generally applicable to calico printing purposes than are the Indigosols. For direct printing on white grounds and for the dyeing of plain shades the Soledons are, doubtless, admirably adapted ; but when it is a question of applying them to the production of resist and discharge styles their affinity for the fibre constitutes a handicap because, although the regeneration of the parent dyestuff (under the printed parts) is prevented, for the moment, by the action of the resisting or discharging agents, its leuco compound, being more or less unaffected by these agents, and being actually dyed on the cloth, is retained *in situ* throughout the operations of oxidation and washing and is liable, subsequently, to develop-up by air-oxidation—if it has not already developed, in part, during the normal oxidation. On the contrary, the Indigosol colours possess no affinity for the fibre ; when printed or padded on cloth they simply exist upon it as soluble salts ; and, when resist colours are printed on padded grounds of Indigosols they displace the ground colour *entirely*, the unoxidised Indigosol washing out readily in process. Hence nothing remains under the illuminating resist colours to develop at a later stage and dull the brightness of the shades.

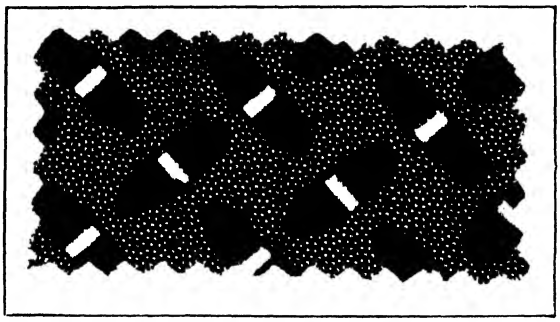
To this distinctive advantage, together with the excellent fastness of the wide range of colours they afford, and to their easy and comprehensive applica-

tion to a variety of old and new styles, the Indigosol dyestuffs owe the favourable reception that has been accorded them by textile printers in all parts of the world.

The Application of Indigosols.—The facility with which the colouring principles of the Indigosols can be developed by a variety of oxidising agents not only connotes great latitude in application, but has led to exhaustive research on processes, with the object of establishing the best methods for particular purposes. During the last few years a spate of more or less practicable recipes and emended recipes has emanated from both manufacturers and consumers of Indigosols, with the result that potential users of these dyestuffs find it somewhat difficult to discriminate between the merits of the bewildering number of suggestions put forward. In the following description of the methods of applying Indigosols, therefore, only those processes which are in current use, or recent modifications of them, will be dealt with in detail.

(a) *The Nitrite Process.*—In this process a thickened solution of the dyestuff along with the requisite amount of nitrite of soda is printed on bleached unprepared cloth, then dried and passed through an acid developing bath in which nitrous acid is evolved from the nitrite of soda and at once regenerates the original vat colour from which the Indigosol was prepared.

In its simplest form the nitrite process is illustrated by the two following patterns:—



(D. & H.)

Dark blue object: Dark Blue O. (below).
White resist: Rongalite C. and Zinc Oxide.
Dark honeycomb ground: Dark Blue O., 2 : 1 reduction.

These patterns were produced as follows:—

WHITE RESIST.

300 grms. Rongalite C. or Formosul.
200 ,, zinc oxide 50 per cent. paste.
600 ,, British gum solution.

Warm to dissolve, cool, and make up to 1000 c.c

DARK BLUE O.

160 grms. Indigosol O.
40 c.c. glycerine.
15 ,, water.

Mix into a paste and add—

750 c.c. starch-tragacanth paste.

1·5 grms. β-naphthol.
1·25 c.c. caustic soda 90° Tw.
15·0 ,, water.

Warm to 120° F., cool, add—

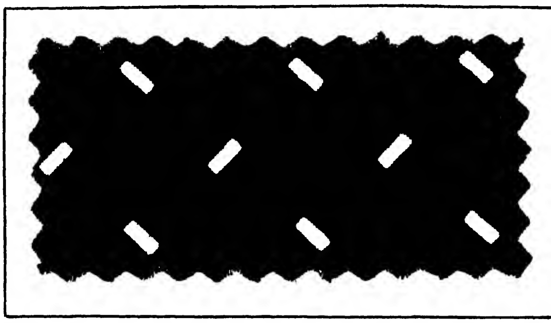
40 grms. nitrite of soda.
100 c.c. water, and make up to 1000 c.c.

Print the white resist and dark blue; dry and overprint, or cover, with the honeycomb ground roller; dry again and develop by passing the goods, at full open width, through the following acid bath:—

$\begin{cases} \text{20 grms. sulphuric acid 168° Tw.,} \\ \text{1000 c.c. water,} \end{cases}$

for 20 seconds at 100° F.; squeeze out excess of liquor, run in air a short time, then wash, soap, wash, and dry.

A similar procedure is carried out in the production of the second pattern, the only differences being that a plain pad roller is used for the overprinting, and the light blue ground printing colour is thickened with gum, which gives a much smoother face than starch thickenings.



Dark blue: Dark Blue O. (above).
White resist: Rongalite and Zinc Oxide (White resist 1 : 1).
Light blue ground: Blue O.K.G., 1 : 8 reduction.

Blue O.K.G.

Exactly as Dark blue O., but thickened with Karaya gum solution instead of with starch-tragacanth paste.

Blue O.K.G., 1 : 8.

1 part Blue O.K.G.
8 parts reduction paste (or gum).

Reduction Paste (or Gum).

$\begin{cases} \text{1000 c.c. starch-tragacanth (or Karaya gum as desired).} \\ \text{7 grms. nitrite of soda.} \\ \text{0·5 ,, soda-ash.} \end{cases}$

Print the dark blue and white resist as before, dry and pad Blue O.K.G. 1 : 8, dry and develop, etc., as already described.

Indigosol O. is rarely used for the two styles just described, being too expensive to compete on favourable terms with the Schlieper-Baum process except in works where the latter process is not employed and where Indigo is printed only occasionally. It is better adapted for special styles, which will be dealt with later.

The foregoing objection does not apply to other and later members of the Indigosol group since, although these are naturally more expensive, in the first instance, than the vat dyestuffs from which they are derived, they offer advantages in practice which compensate, in other directions, for their higher initial cost. When applied by the *nitrite and other wet developing processes* (which allow of the Indigosols being developed without the use of steam) they eliminate entirely the employment of costly agers and, with them, the difficulties that arise from variations in steaming conditions, the necessity for adjusting the output of the printing machines to the capacity of the agers, and the

employment of alkaline printing colours containing reducing agents, which are liable to deteriorate if the printed goods are allowed to lie any length of time before steaming.

Goods printed with Indigosols by these later processes may be stored for lengthy periods before development, provided they are reasonably protected from acid fumes and direct sunlight. On the other hand, if printed by one of the *steam* processes, it is advisable to steam the goods as soon as possible after printing, although there is little risk of premature oxidation if the proper precautions are observed in storing. An important property of Indigosols printed by a steam process is that the colouring matter is completely regenerated on the fibre by ageing or steaming, and requires no further treatment for its development—no chroming or soaping—such as is demanded by ordinary vat dyestuffs. For such articles as linings, small sprig or spot patterns, fine checks and similar small patterns, this is a great advantage as the goods can be sent direct from the steamer for finishing processes without any preliminary washing or soaping. For heavy patterns, of course, the goods, in most cases, require washing and soaping if only to get rid of the thickening materials used in printing.

Most of the Indigosols of the later types are rather less soluble in water than their prototype, Indigosol O., but they are none the less readily dissolved by means of suitable assistants, and except in one or two cases, they all conform to general methods of application. The group now comprises twenty-seven members and includes a full range of colours derived from various classes of vat dyestuffs. The colour letters are prefixed with the following letters, indicating the classes to which they belong, thus:—

O., representing derivatives of Indigo;
I., ,, ,, the Indanthrene series;
A., ,, ,, ,, Algole series;
H., ,, ,, ,, Helindone series.

The range consists of:—

Indigosol Golden Yellow I.G.K.	Indigosol Violet A.Z.B.
,, ,, ,, I.R.K.	,, H.B.
,, Yellow H.C.G.	,, A.Z.G.
,, Orange H.R.	,, O. 6 B.
,, Scarlet I.B.	,, O. 4 B.
,, Pink I.R. extra	,, O.R.
,, Brilliant Pink I. 3 B.	,, O.
,, Red H.R.	,, Green I.B.A.
,, Printing Purple I.R.	,, Green A.B.
,, Red Violet I.R.H.	,, Brown I.R.R.D.
,, Printing Violet I.B.B.F.	,, Printing Black I.B.
,, ,, Blue I.B.	,, Scarlet H.B.
,, ,, Blue I.G.G.	,, Grey I.B.L.
,, Blue I.B.C.	

The solvents used in making-up the printing colours are the following:—

Solution Salt B. (benzyl-sulphanilate of soda).
Fibrit D. (diethylene glycol).
Glyecine A. (thiodiglycol).
Developer D. (diethyl tartrate).
Developer G.A. (ethylene glycol).
Acetine.
Fixer C.D.H. (urea).
Dehapan O. (urea and cresylic acid).

The nitrite process, as applied to the printing of the foregoing Indigosols, is carried out as follows:—

TYPICAL PRINTING COLOURS (NITRITE PROCESS).

	1.	2.	3.	4.	5.	6.	7.	8.
Indigosol Golden Yellow I.G.K.	50	..	..	..	..	..	..	..
,, Orange H.R.	..	60	..	..	..	..	..	..
,, Scarlet I.B.	..	..	80	..	..	..	..	..
,, Printing Purple I.R.	..	..	..	70	..	..	..	..
,, Printing Blue I.B.	..	..	..	..	60	..	..	..
,, O. 4 B.	..	..	..	..	..	50	..	..
,, Green I.B.A.	..	..	..	..	..	..	80	..
,, Printing Black I.B.	..	..	..	..	..	..	..	125
Solution Salt B.	..	50	..	..	..	..	..	..
Fibrit D.	70	50	..	..	..	..	..	..
Glyecine A.	50	..	..	50	30	..	..	..
Indigosol Developer D.	..	..	..	..	..	50	50	..
Fixer C.D.H.	60	..	..	..	..	..	..	..
Acetine	..	..	50	..	..	..	..	30
Soda-ash	2	2	2	4	2	2	2	2
Water	248	208	243	216	228	358	248	343
Starch-tragacanth paste (neutral)	500	500	600	600	650	510	600	460
Warm till dissolved, cool, and add:								
Sodium nitrite sol. 30 per cent.	20	130	25	60	30	30	20	40
	1000 parts.							

All Indigosols may be printed by these formulæ or modifications of them, any necessary alterations in the quantities of the components being easily ascertained by experiment.

During the past year the introduction of a new combined solvent, Dehapan O., has greatly simplified the preparation of Indigosol printing colours. It is suitable for use with all processes and can replace all the solvents previously used. The table given below illustrates its application to the nitrite process.

INDIGOSOL PRINTING COLOURS WITH DEHAPAN O. (NITRITE PROCESS).

	1.	2.	3.	4.	5.	6.
Indigosol Golden Yellow I.G.K.	50	..	..	..	..	..
,, Pink I.R. extra	..	40	..	..	..	..
,, Printing Violet I.B.B.F.	..	..	80	..	..	..
,, H.B.	..	..	..	60	..	..
,, Green A.B.	..	..	..	..	80	..
,, Brown I.R.R.D.	..	..	..	..	..	40
Dehapan O.	150	200	100	200	100	300
Water	250	160	250	170	250	90
Starch-tragacanth paste (neutral)	500	500	500	500	500	500
Heat till dissolved, then add:						
Soda-ash 10 per cent. solution	20	20	20	20	20	20
Sodium nitrite 30 per cent. solution	30	80	50	50	50	50
	1000	1000	1000	1000	1000	1000

All nitrite of soda printing colours may be reduced in shade by additions of the reduction paste given under Indigosol O.

After printing, the dried goods are passed through a developing bath of sulphuric acid (20 grms. H_2SO_4, 168° Tw., per litre) at 65°–75° C. The duration of the passage may vary from 2 to 20 seconds, but if the goods are immersed for less than 6 seconds they must be run in air (immediately after squeezing out of the acid bath) for at least 20 seconds in order to complete the oxidation of the dyestuff. They are then washed and soaped.

(b) *The Bichromate Process.*—This process is an alternative to the nitrite process and more used, perhaps, for Indigosol resists under Aniline black than for direct printed styles. It may, however, be employed for the latter, the colours being made-up as in the tables below.

PRINTING COLOURS (BICHROMATE PROCESS).

	1.	2.	3.	4.	5.	6.
Indigosol Golden Yellow I.R.K.	60	..	..	..	..	..
„ Orange H.R.	..	60	..	..	..	..
„ Pink I.R. extra	..	..	30	..	..	..
„ Printing Blue I.G.G.	..	..	..	60	..	..
„ O. 4 B.	..	..	..	..	50	..
„ Brown I.R.R.D.	..	..	..	..	..	40
Glyecine A.	60	..	..	..	..	..
Solution Salt B.	..	..	..	..	..	50
Indigosol Developer D.	30	..	..	..	..	60
Fibrit D.	..	40	50	..	..	..
Acetine	..	50	50	30	30	..
Warm water	250	200	210	260	220	250
Starch-tragacanth paste (neutral)	600	630	660	650	700	600
Warm till dissolved, cool, and add:						
Ammonium vanadate 1 per cent. solution	..	20	..	..	..	..
	1000 parts.					

Indigosol pink I. 3 B. requires an addition of 10 grms. of bichromate of soda per 60 grms. dyestuff, 80 grms. Glyecine A., and 10 grms. ammonium vanadate; other colours, for padding purposes, also require additions of copper sulphate, ammonium oxalate, oxalic acid, or nitrite of soda in order to obtain their best yield.

The number of special solvents and the various modifications of recipe involved in the working of the bichromate process have been the cause of complaint on the part of users of Indigosols. The manufacturers have now, however, overcome the objections by employing Dehapan O. in place of the earlier solvents and other adjuncts, thus simplifying the recipes and saving a good deal of time, trouble, and expense in the colour shop and "drug" room. The table opposite illustrates a few typical examples of the improved recipes.

All other Indigosols may be made-up on the lines of No. 1 opposite, varying the amount of Dehapan O. from 30 grms. for 60 grms. of Indigosol yellow H.C.G. to 250 grms. for 40 grms. of Indigosol brown I.R.R.D., the actual amount required being determined by the solubility of the particular Indigosol employed.

PRINTING COLOURS WITH DEHAPAN O. (BICHROMATE PROCESS).

	1.	2.	3.	4.	5.	6.
Indigosol Golden Yellow I.G.K.	50	..	..	..	..	..
,, Brilliant Pink I. 3 B.	..	60	..	..	..	..
,, Red H.R.	..	..	60	..	..	..
,, Printing Violet I.B.B.F.	..	..	..	80	..	..
,, O. 4 B.	..	..	..	..	50	..
,, Green I.B.A.	..	..	..	..	..	100
Dehapan O.	100	100	..	50	..	100
Water	350	90	410	360	450	300
Starch-tragacanth paste (neutral)	500	500	500	500	500	500
Heat till dissolved, then add:						
Soda-ash 10 per cent. solution	..	50	..	..	..	..
Bichromate of soda 10 per cent. solution	..	200	..	..	..	..
Oxalate of ammonia	..	..	30	..	..	..
Oxalic acid	..	..	..	10	..	..
	1000 parts.					

The development of the printed colours is effected by a short passage through a bath of chromic acid made up as follows:—

30 grms. bichromate of soda.
80 ,, sulphuric acid 168° Tw.
1000 c.c. water.

The printed goods are passed through this bath for 1–2 seconds at 95°–100° F., allowed to run in air over a series of rollers for 20–40 seconds, then washed well and soaped as usual for vat dyestuffs.

If desired, the development may be carried out in the first compartment of the open soaper. Sufficient developing liquor is added to cover the bottom rollers only; the speed of the machine is arranged to give a passage of 6–10 seconds at 95°–100° F., and complete development of the colour is obtained without giving any other air passage than that afforded by the running of the cloth over and under the top and bottom rollers, respectively. Washing and soaping follow in the remaining compartments of the machine, the whole process being continuous.

(c) *The Chlorate of Alumina Process.*—This process differs from all other processes of printing Indigosols in that the development of the colour is dependent neither upon steaming nor a passage through an oxidising bath, but is brought about simply by allowing the goods to lie exposed for several hours. The colours are printed, according to the formulæ given below, on cloth prepared with ammonium vanadate and tartaric acid. After drying, the printed goods are allowed to lie overnight (12–14 hours), during which period the aluminium chlorate dissociates and completely oxidises the Indigosol dyestuff. No further treatment of the goods is necessary, except the usual washing and soaping.

The cloth is prepared by padding in a solution of—

1 grm. ammonium vanadate,
5 grms. tartaric acid,
1000 c.c. water,

and dried in the hot flue.

On cloth so prepared the following colours may be printed:—

	1.	2.	3.	4.	5.	6.	7.
Indigosol Golden Yellow I.G.K.	50	..	..	..	..	..	..
,, Orange H.R.	..	60	..	..	..	..	..
,, Brilliant Pink I. 3 B.	..	..	60	..	..	..	..
,, Printing Purple I.R.	..	..	..	60	..	..	..
,, ,, Blue I.G.G.	..	..	..	..	60	..	..
,, O.	..	..	..	..	..	80	..
,, Green I.B.	..	..	..	..	..	..	80
Solution Salt B.	..	50	..	..	..	..	..
Glyecine A.	60	60	60	60	60	60	60
Mix well and add:							
Water (Hot)	285	230	250	250	280	260	250
Starch-tragacanth paste	550	550	550	550	550	550	550
Heat till dissolved, cool to 100° F., and add:—							
Tartaric acid 10 per cent. solution	20	20	30	30	20	20	20
Chlorate of alumina 42° Tw.	30	30	50	50	30	30	30
Ammonia 25 per cent.	..	..	..	..	..	..	10
Acetate of soda	5	..	..	..	..	..	..
	1000 parts.						

REDUCTION PASTE.

900 grms. starch-tragacanth paste.
50 ,, Glyecine A.
20 ,, water.
10 ,, tartaric acid 10 per cent.
20 ,, chlorate of alumina 42° Tw.

1000

Print, dry, allow to lie exposed to air for 12–14 hours (overnight), wash, and soap.

Other Indigosols are made up similarly.

As a method for the easy fixation of Indigosols the aluminium chlorate process may be very convenient for spray and screen printers and some of the smaller block printers who have not always steaming, developing, and washing apparatus available, but for general industrial work in bulk it could, conceivably, easily lead to irregular results and, in any case, it is a process not readily controlled and of a somewhat aleatory nature.

Steaming Processes.—For the direct printing of multicolour patterns in which Indigosol dyestuffs are associated with other colouring matters of entirely different properties and modes of application—Chrome colours, Rapid Fast colours, Aniline black, Azoic bases on naphthol prepares, etc.—the steaming processes are the most convenient and are adaptable to a greater variety of such styles than are the wet-developing processes. As direct printed styles constitute by far the greatest proportion of the output of most printworks, the importance, in the case of Indigosols, of a method of development which works in with the methods employed for the fixation, or production on the fibre, of other types of dyestuffs, will readily be appreciated.

The recipes given in Table (A.) below are suitable for the steam development of all Indigosol dyestuffs.

(A.) STEAM DEVELOPMENT: DEVELOPER D. PROCESS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Indigosol Yellow H.C.G.	6	..	..	..	..	..	..	..	..	..	..
„ Golden Yellow I.G.K.	..	5	..	..	..	..	..	..	..	..	..
„ „ „ I.R.K.	..	..	6	..	..	..	..	..	..	..	..
„ Orange H.R.	..	..	..	6	..	..	..	..	..	..	..
„ Scarlet I.B.	..	..	..	..	8	..	..	..	..	..	..
„ „ H.B.	..	..	..	..	..	4	..	..	..	..	..
„ Pink I.R. extra	..	..	..	..	..	..	3	..	..	..	..
„ Brilliant Pink I. 3 B.	..	..	..	..	..	..	..	6	..	..	..
„ Red H.R.	..	..	..	..	..	..	..	..	6	..	..
„ Printing Purple I.R.	..	..	..	..	..	..	..	..	..	6	..
„ Red Violet I.R.H.	..	..	..	..	..	..	..	..	..	..	4
Indigosol Developer D.	4	4	3	4	4	6	6	3	4	5	6
Dehapan O.	..	5	10	3	3	5	5	..	..	..	5
Starch-tragacanth thickening, not neutralised	50	50	50	50	50	50	50	50	50	50	50
Water	28	24	25	26	23	16	17	20·5	28	22	27
Heat until dissolved, then add whilst hot:—											
Chlorate of soda 10 per cent.	8	8	4	8	8	15	15	18	8	15	4
Cool, and add:—											
Vanadate 1 per cent.	2	3	1	2	2	4	4	2	2	2	2
Ammonia	2	1	1	1	2	..	..	0·5	2	..	2
	100 parts.										

	12.	13.	14.	15.	16.	17.	18.	19.	20.	21.
Indigosol Violet A.Z.B.	8	..	..	..	..	..	..	..	..	..
„ Printing Violet I.B.B.F.	..	8	..	..	..	..	..	..	..	..
„ H.B.	..	..	6	..	..	..	..	..	..	..
„ Printing Blue I.B.	..	..	..	6	..	..	..	..	..	..
„ „ „ I.G.G.	..	..	..	..	6	..	..	..	..	..
„ O. 6 B.	..	..	..	..	..	5	..	..	..	..
„ O. 4 B.	..	..	..	..	..	..	5	..	..	..
„ Green A.B.	..	..	..	..	..	..	..	8	..	..
„ Brown I.R.R.D.	..	..	..	..	..	..	..	..	4	..
„ Printing Black I.B.	..	..	..	..	..	..	..	..	..	12
Indigosol Developer D.	4	4	4	2	2	4	4	4	6	4
Dehapan O.	..	1	5	..	..	..	..	5	5	..
Starch-tragacanth thickening, not neutralised	50	50	50	50	50	50	50	50	50	40
Water	28	19	24	33	32	30	30	19	21	16
Heat until dissolved, then add whilst hot:—										
Chlorate of soda 10 per cent.	6	15	8	6	6	8	8	10	10	25
Cool, and add:—										
Vanadate 1 per cent.	2	1	2	2	2	2	2	3	1	1
Ammonia	2	2	1	1	2	1	1	1	3	2
	100 parts.									

The older steaming methods, which involved the use of a large number of special solvents and acid-yielding developers (many of them proprietary articles), were not only cumbersome and complicated, but also entailed the holding of a stock of expensive materials. For most purposes these have now been discarded in favour of the newer methods described here, in which all solvents previously used are replaced by Dehapan O. In a few mixed styles older recipes are still occasionally used, and these will receive attention elsewhere in dealing with such styles.

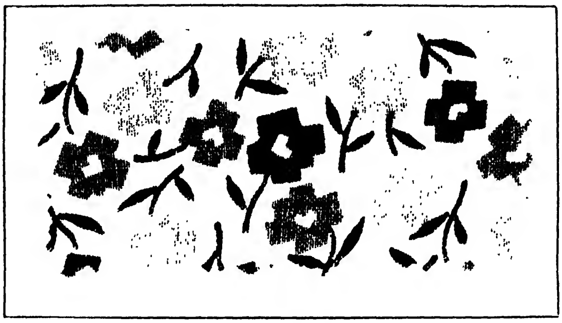
For Indigosol brown I.R.R.D. it is advisable to beat-up the colouring matter with a little water and a portion of the Developer D., then to the paste thus formed add the remainder of the ingredients, mix well for a time and, without heating, strain the colour through fine straining cloths.

Sulphocyanide of ammonia, being cheaper than Indigosol Developer D. (diethyl tartrate), may replace the latter as the acid component in the printing colours.

(B.) STEAM DEVELOPMENT: SULPHOCYANIDE PROCESS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Indigosol Golden Yellow I.G.K.	5	..	..	..	..	..	..	..	..	..	..	..
„ „ „ I.R.K.	..	6	..	..	..	..	..	..	..	..	..	..
„ Orange H.R.	..	..	6	..	..	..	..	..	..	..	..	..
„ Scarlet H.B.	..	..	..	4	..	..	..	..	..	..	..	..
„ Pink I.R. extra	..	..	..	..	3	..	..	..	..	..	..	..
„ Brilliant Pink I. 3 B.	..	..	..	..	..	6	..	..	..	..	..	..
„ Printing Purple I.R.	..	..	..	..	..	..	6	..	..	..	..	..
„ „ Violet I.B.B.F.	..	..	..	..	..	..	..	8	..	..	..	..
„ H.B.	..	..	..	..	..	..	..	..	5	..	..	..
„ O. 6 B.	..	..	..	..	..	..	..	..	..	5	..	..
„ Green I.B.A.	..	..	..	..	..	..	..	..	..	..	10	..
„ „ A.B.	..	..	..	..	..	..	..	..	..	..	..	8
Dehapan O.	5	10	10	20	20	..	..	10	15	..	10	20
Starch-tragacanth thickening, not neutralised	50	50	50	50	50	50	50	50	50	50	50	50
Water	34	27·5	21	10	11	25	21	15	16	28	9	6
Heat until dissolved, add:—												
Chlorate of soda 10 per cent.	4	4	8	10	10	12	16	12	8	10	12	10
Sulphocyanide of ammonia 1 : 1	1·5	2	4	4	4	4	5	4	4	6	6	5
Cool, and add:—												
Vanadate 1 per cent.	0·5	0·5	1	2	2	2	1	1	1	1	1	1
Ammonia	..	..	..	..	..	1	1	..	1	..	2	..
	100 parts.											

The pattern herewith has been printed with the colours stated, following Tables (A) and (B) :—



Multicolour pattern with Indigosols (D. & H.).

Yellow:—6	per cent.	Indigosol	Golden Yellow I.R.K.	(No. 2, Table (B.).)
Red:—3	,,	,,	Pink I.R. extra	(,, 5, ,, (B.).)
Violet :—1	,,	,,	Printing Purple I.R.	(,, 7, ,, (B), reduced 1: 5.)
Green:—8	,,	,,	Green A.B.	(,, 19, ,, (A.).)

Reduction Pastes (Tables (A.) and (B.)).

	(A.)	(B.)
Neutral tragacanth thickening 6 per cent.	860 grms.	860 grms.
Indigosol Developer D.	9 ,,	.. ,,
Sulphocyanide of ammonia 1 : 1	.. ,,	15 ,,
Chlorate of soda 10 per cent.	15 ,,	25 ,,
Ammonium vanadate 1 : 1000	100 ,,	100 ,,
Water	16 ,,	— ,,
	1000	1000

The goods, printed as described, are dried and steamed in the rapid ager for 8–15 minutes (twice through), then washed and soaped at the boil. (In the Mather & Platt, and the John Wood, continuous automatic ageing and steaming machines the steaming period can be adjusted as required and carried out at a single operation, thus effecting a saving in time and labour.)

Short Steaming Process.—In order to ensure complete oxidation of the Indigosols by the foregoing steaming processes it is essential to give a passage of at least 8 minutes in the ager, and a longer passage (or a second) is by no means infrequently necessary. With a view to shortening the process, and increasing production, the makers of Indigosols have worked out an improved process by means of which it is now possible to develop the colours completely by an ageing of 2 minutes only. At the same time a longer ageing may be given without detriment—a great advantage in cases where Indigosols are printed along with Chrome colours or on certain qualities of viscose silk. Moreover, the recipes have been considerably simplified and the printing colours are of good stability, keeping in perfect condition for 14 days with the exception of Indigosol Green A.B. and Printing Blue I.B., which keep good only for a week at most.

The goods are printed with the following colours :—

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.	13.
Indigosol Yellow H.C.G.	6	..	..	..	..	..	..	..	..	..	..	..	..
,, Golden Yellow I.G.K.	..	5	..	..	..	..	..	..	..	..	..	..	..
,, ,, ,, I.R.K.	..	..	6	..	..	..	..	..	..	..	..	..	..
,, Orange H.R.	..	..	..	6	..	..	..	..	..	..	..	..	..
,, Scarlet I.B.	..	..	..	..	8	..	..	..	..	..	..	..	..
,, ,, H.B.	..	..	..	..	..	4	..	..	..	..	..	..	..
,, Pink I.R. extra	..	..	..	..	..	..	3	..	..	..	..	..	..
,, Brilliant Pink I. 3 B.	..	..	..	..	..	..	..	6	..	..	..	..	..
,, Red H.R.	..	..	..	..	..	..	..	..	6	..	..	..	..
,, Printing Purple I.R.	..	..	..	..	..	..	..	..	..	6	..	..	..
,, Red Violet I.R.H.	..	..	..	..	..	..	..	..	..	..	4	..	..
,, Violet A.Z.B.	..	..	..	..	..	..	..	..	..	..	..	8	..
,, Printing Violet I.B.B.F.	..	..	..	..	..	..	..	..	..	..	..	..	8
Glyceine A.	..	..	5	..	..	..	..	..	..	..	..	..	..
Dehapan O.	..	20	15	10	5	10	20	..	5	5	20	..	..
Hot water	35	16	11	19	24	18	9	19	17	17	1	24	17
with													
Starch-tragacanth	55	55	55	55	55	55	55	55	55	55	55	55	55
Dissolve hot and add hot:—													
Ammonium chlorate 23° Tw.	3	3	3	5	3	8	8	15	12	12	15	8	15
Cool and add:—													
Vanadate 1 per cent.	1	1	5	5	5	5	5	5	5	5	5	5	5
	100 parts.												

	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.	24.	25.	26.
Indigosol H.B.	5	..	..	..	..	..	..	..	..	..	..	..	..
,, Printing Blue I.B.	..	6	..	..	..	..	..	..	..	..	..	..	..
,, A.Z.G.	..	..	5	..	..	..	..	..	..	..	..	..	..
,, Printing Blue I.G.G.	..	..	..	6	..	..	..	..	..	..	..	..	..
,, O. 6 B.	..	..	..	..	5	..	..	..	..	..	..	..	..
,, O. 4 B.	..	..	..	..	..	5	..	..	..	..	..	..	..
,, O.R.	..	..	..	..	..	..	6	..	..	..	..	..	..
,, O. extra	..	..	..	..	..	..	..	5	..	..	..	..	..
,, Green I.B.A. paste	..	..	..	..	..	..	..	..	10	..	..	..	..
,, ,, A.B.	..	..	..	..	..	..	..	..	..	8	..	..	..
* ,, Brown I.R.R.D.	..	..	..	..	..	..	..	..	..	..	4	..	..
,, Grey I.B.L.	..	..	..	..	..	..	..	..	..	..	..	6	..
,, Printing Black I.B.	..	..	..	..	..	..	..	..	..	..	..	..	12
Dehapan O.	10	5	5	..	..	..	..	..	5	15	30	5	..
Hot water	17	28	22	26	27	27	35	36	27	16	..	21	27
with													
Starch-tragacanth	55	55	55	55	55	55	55	55	55	55	53	55	55
Dissolve hot and add hot:—													
Ammonium chlorate 23° Tw.	8	5	8	8	8	8	3	3	2	5	8	8	5
Cool and add:—													
Vanadate 1 per cent.	5	1	5	5	5	5	1	1	1	1	5	5	1
	100 parts.												

* Indigosol Brown I.R.R.D. is made up in the cold as described in Table (A), p. 409.

Reduction Pastes.	(1.)	(2.)
Tragacanth thickening 8 : 100.	700 grms.	700 grms.
Ammonium vanadate 1 per cent.	30 „	5 „
Ammonium chlorate 23° Tw.	100 „	20 „
Water	165 „	265 „
Ammonia 25 per cent.	5 „	10 „
	1000	1000

Paste (1) is employed for reducing the majority of the foregoing printing colours, but paste (2) for Indigosol Golden Yellows I.G.K. and I.R.K., Yellow H.C.G., and Green I.B.A.

Ammonium Chlorate 23° Tw.

(1) {323 grms. barium chlorate.
400 c.c. boiling water.

(2) {133 grms. ammonium sulphate.
450 c.c. boiling water.

Add (2) to (1), allow to settle, decant the clear liquor and set at 23° Tw. After printing, dry, steam for 2 minutes (or longer if required), wash, soap at the boil, wash, and dry.

Indigosols with Chrome Colours.—Apart from vat colour specialities, cretonnes and other furnishing fabrics are printed, as a rule, with Chrome mordant colours and Alizarin reds and pinks. These latter demand a previous preparation of the cloth with oleine and require at least an hour's steaming for their full development, whereas Chrome colours are better without oleine and can be fixed perfectly, in most cases, by a short steaming of ten minutes. On oil-prepared cloth the fastness to light of Chrome blues, violets, and greens is much inferior to that of other Chrome colours and, in any case, it is not too good. In these circumstances the Indigosols provide excellent and fast substitutes for the weaker members of the Chrome colour group and, made up according to the recipes given below, may be printed along with any ordinary fast Chrome colours and steamed either for ten minutes only, or for an hour, according to requirements. Indigosol pink I.R. and other reds and scarlets may be used in place of Alizarin red and pink and thus shorten the duration of steaming and obviate the necessity for the preparation with oleine.

The Indigosols that come chiefly into consideration for this purpose are:

Indigosol Red Violet I.R.H. (A. 80).
„ O. 4 B. (A. 50).
„ Printing Blue I.G.G. (C. 60).
Indigosol Printing Violet I.B.B.F. (B. 80).
Indigosol Pink I.R. extra (B. 30).
„ Green I.B.A. (B. 80).

The letters and figures in brackets (A. 80, etc.) refer to the recipes given below; thus (A. 80) signifies Recipe (A): 80 grammes of dyestuff per kilo. of printing colour.

	(*A.*)	(*B.*)	(*C.*)
Dyestuff		As above.	
Neutral starch-tragacanth paste	600	600	600
Glyecine A.	..	50	50
Solution Salt B.	..	30	..
Water	200	100	200
Chlorate of soda 10 per cent.	40	100	60
Ammonium sulphocyanide 1 : 1	20	30	20
Ammonium vanadate 1 per cent.	10	10	10
Make up to :—		1000 parts.	

For the production of fairly fast greens, olives, and chocolates missing from the Chrome colour and Indigosol ranges, *mixtures* of suitable members of the two ranges may be used to fill in the gaps. Care must be taken to reduce the basicity of the chromium acetate in the Chrome colour component by the addition of a salt which splits off acid on steaming, otherwise the basic acetate formed will resist the Indigosol to some extent, or rather prevent its full development. Suitable salts for this purpose are ammonium sulphocyanide and ammonium sulphate. The latter is the more generally useful, as the sulphocyanide precipitates some Chrome colours.

Typical recipes for mixtures of Chromocitronine R. and Chrome fast xanthine 2 R. with Indigosols (Chlorate process) are given below:—

Chrome Printing Colour.

40	grms.	Chromocitronine R. or Chrome fast xanthine 2 R.
250	,,	water.
500	,,	starch-tragacanth paste.
50	,,	ammonium sulphate.
160	,,	acetate of chromium 24° Tw.
1000		

Indigosol Printing Colour.

60	grms.	Indigosol dyestuff.
30	,,	glycerine.
300	,,	water.
500	,,	starch-tragacanth paste.

Heat until dissolved, cool a little, and add—

30	grms.	ammonium sulphocyanide.
20	,,	sodium chlorate.
50	,,	water.
10	,,	ammonium vanadate 1 per cent. solution.
1000		

The Indigosols used for mixing with the above two chrome colours for greens, olives, and chocolates are usually:

Indigosol O. 4 B.	Indigosol H.B. (requires 50 grms. Dissolving Salt B.).
,, A.Z.G.	,, Violet A.Z.B. (75 grms. per kilo.).
,, O. 6 B.	,, Green A.B.
	,, Red Violet I.R.H.

The Indigosol and Chrome colours mixed in various proportions are printed, dried, steamed for 10 minutes, washed, and soaped as usual.

If these mixtures are printed in light shades—say reduced 1 : 4—the amount of reducing paste corresponding to the Chrome colour content requires an addition of $2\frac{1}{2}$ per cent. of ammonium sulphate.

Thus:—

$\frac{3}{1}$ C. I. Green 1 : 4.

150	grms.	Chromocitronine R. printing colour, as before.
50	,,	Indigosol O. 6 B. printing colour, as before.
800	,,	starch-tragacanth paste.
15	,,	ammonium sulphate.

600 grammes of starch-tragacanth reducing paste out of the total of 800 grammes used correspond to the 150 grammes of Chromocitronine R. printing colour, and therefore 15 grammes of ammonium sulphate are required to provide the acidic conditions demanded by the Indigosol.

Indigosols with Rapid Fast Colours.—In a similar manner the Indigosols can be printed, either by the steam process described for Chrome colours or by the nitrite process, along with Rapid Fast colours in multicolour patterns. By the nitrite process the Indigosols can also be *mixed* with the Rapid Fast colours for shading purposes, but by the steaming process this is not possible.

(a) *Steaming Process.*—In this process the goods are simply printed with the Indigosols described on page 412 and with Rapid Fast colours made up by the usual recipe (*q.v.*); they are then dried and steamed for 3 minutes to develop the Indigosols; thereafter they are passed through a bath of

30 c.c. acetic acid 50 per cent.,
50 grms. sulphate of soda,
1000 c.c. water

at 160°-180° F. to develop the Rapid Fast colours, finally being washed and soaped at the boil.

(b) *Nitrite Process.*—In this the goods are similarly printed with ordinary Rapid Fast colours and with Indigosols (nitrite recipe) either singly, or mixed together for compound shades; they are then aged with moist steam in the rapid ager and developed in the open soaper with formic or oxalic acid or a mixture of the two.

Developing Baths.	(1)	(2)	(3)
Formic acid 90 per cent.	40 c.c.	..	15 c.c.
Oxalic acid	..	30 grms.	10 grms.
Common salt	80 grms.	80 ,,	80 ,,
Water	1000 c.c.	1000 c.c.	1000 c.c.

The duration of passage through the developer is 20–30 seconds, temperature 180°–190° F. The goods are finally washed and soaped at the boil. It should be noted that the Indigosol printing colours require a minimum of 12 grammes of nitrite of soda per kilo. for this process whatever their shade.

The Indigosols may also be printed alongside **Rapidogen colours,** which resemble Rapid Fast colours in general properties and application. The Rapidogen colours are, however, rather severely attacked by the acid passage necessary for the development of the Indigosols and require an addition of zinc oxide to the printing colours to counteract the destructive action of the acid. Made-up according to the following typical recipes, however, they withstand the acid treatment and yield the full beauty of their exceptionally brilliant shades:—

	1.	2.	3.	4.	5.	6.
Rapidogen Yellow G.	80	..	..	..	..	..
,, Orange G.	..	80	..	..	..	..
,, Scarlet R.	..	..	80	..	..	..
,, Bordeaux R.	..	..	..	80	..	..
,, Blue B.	..	..	..	..	45	..
,, Violet B.	..	..	..	..	..	45
Water	260	280	260	230	215	255
Caustic soda 72° Tw.	30	30	30	30	30	30
Methylated spirit	30	30	30	30	30	30
Neutral starch-tragacanth thickening	500	500	500	550	500	500
Zinc white 1 : 1	100	80	100	30	100	140
Glyecine A.	..	..	..	..	30	..
Urea	..	..	..	..	50	..
Neutral chromate solution	..	..	..	50	..	..
	1000					

Reduction Mixture.

Neutral tragacanth thickening	800
Water	110
Caustic soda 72° Tw.	20
Zinc white 1:1	70
	1000

Neutral Chromate Solution.

150 grms. bichromate of soda dissolved in
700 c.c. water, adding
150 c.c. caustic soda 62° Tw.

To 1 litre

The zinc oxide in these colours may be replaced wholly or in part by burnt magnesia (MgO).

The goods having been printed with the foregoing Rapidogens, along with any Indigosols (nitrite-Dehapan recipe), are passed, in the open width, through No. 3 developing bath (p. 415) (formic-oxalic acid) for about 2 seconds at 190° F.; they are then given an air passage over rollers, or on a " creeper," for 20–30 seconds, and finally washed thoroughly and soaped at the boil.

An alternative method is to steam the printed goods 4–5 minutes in a Mather-Platt ager in an atmosphere of acetic acid, which develops fully the Rapidogens and renders them immune to the effect of the acid bath (even sulphuric acid) required for the development of the Indigosols. For this process Rapidogen colours *without* zinc oxide may be used; but the Indigosol recipes require about three times the normal quantity of nitrite of soda to regenerate fully the colouring matter.

Indigosols on Naphthol Prepares along with Azoic Colours.—In this style various Indigosol blues, greens, yellows, and violets play the same rôle as in the case of Rapid Fast and Rapidogen colours; they supply the missing links in the chain of bright shades provided by the Fast colour salts and bases printed on naphthol-prepared cloth.

The style may be executed either by the nitrite or steam development method, the nitrite method being the better. The acid treatment has little or no effect on the brilliancy of Azoic colours on Naphthol A.S., whereas steaming dulls the shades of many of them considerably. If oxalic acid is used for developing the Indigosols, about double the quantity of nitrite of soda is required in the printing colour than if sulphuric is used; otherwise the process is the same. Typical recipes for the Indigosols generally used are given in the table below:

(a) *Oxalic Acid Development.*—The following are typical recipes for Indigosol (nitrite) colours for oxalic acid development:—

Indigosol Yellow H.C.G.	60	..	..	..	..	..
,, Golden Yellow I.G.K.	..	50	..	..	..	..
,, O.R.	..	..	60	..	..	..
,, O.	..	..	..	80	..	..
,, Green I.B. (or I.B.A.)	..	..	..	..	80	..
,, Printing Black I.B.	..	..	..	..	..	120
Glycecine A.	50	50	50	50	50	50
Solvay soda	2	2	2	2	2	2
Water	238	248	238	218	218	168
Starch-tragacanth thickening, neutralised with ammonia until faintly alkaline	600	600	600	600	600	600
Heat until dissolved, cool, and add:—						
Nitrite 1 : 2	50	50	50	50	50	60
	100 parts.					

Reducing Paste.

Tragacanth thickening 6 per cent.	800
Water	180
Nitrite 1 : 2	20
	1000

The goods, after printing with the above colours and appropriate diazotised colour bases (on naphthol-prepared cloth), are passed for 1–2 seconds through a bath containing 30 grms. of oxalic acid per litre at a temperature of 70° F.; they are then given an air-run of 30 seconds, after which they are washed and soaped at the boil as usual.

The foregoing formulæ may also be used for Indigosol O. 4 B. and O. 6 B., and Indigosol printing blues I.B. and I.G.G., but the temperature of the developing bath must be increased to 160° F. for these dyestuffs.

Any impurity in the white ground, after development, is easily remedied by a short treatment in boiling caustic soda, 1½° Tw., followed by the usual washing and soaping.

(b) *Sulphuric Acid Development.*—A printed pattern illustrating this method of working Indigosols in conjunction with Azoic bases, together with a detailed description of its means of production, will be found in the section dealing with Naphthol A.S.

(c) A process based on the use of lead chromate along with hydrochloric acid development has been put forward, but it yields inferior results and is of little practical interest.

(d) *Steam Process.*—In this process, Indigosol colours, made up with chlorate of soda and oxalate of ammonia according to the recipe given under "Variamine blue Resists," are printed on naphtholated cloth along with Azoic colours. The printed cloth is then steamed for 8 minutes in the rapid ager, and washed and soaped as usual.

(e) A similar process which, however, obviates steaming, is carried out by printing Indigosol colours containing sulphate and chlorate of alumina and Azoic colours on naphthol-prepared cloth. Instead of steaming to develop the Indigosols, the goods are allowed to lie exposed overnight, during which period the colours become fully oxidised. If white grounds are required, the goods are then simply washed and soaped; if coloured grounds are required they are first padded through a suitable diazo solution, *e.g.* Variamine blue, and subsequently treated as described later under "Variamine blue Resists."

Indigosols in Reserve and Discharge Styles.—The Indigosols are easily developed by gentle oxidation, and they are as easily prevented from developing by alkalies and reducing agents; but reducing agents do not *destroy* them and, under suitable conditions, the Indigosols can be developed in the presence of such bodies as hydrosulphites, sulphites, and bisulphites or, at least, Indigosol printing colours which, at the outset, contained such reducing agents can subsequently be developed without much, if any, loss of tinctorial strength. These properties of the Indigosols, together with the excellent general fastness and extensive chromatic range of the group, have made it possible to introduce a number of new and fast resist and discharge styles, and to improve the quality of several older styles in respect both of fastness and of the variety of colour effects obtainable. Among the more important of these applications of Indigosols, the following may be cited in illustration of their manifold possibilities:—

(*a*) Fast Indigosol resist colours on Aniline black grounds,
(*b*) „ „ „ „ dyed vat colour grounds,
(*c*) „ „ „ „ Azoic colour grounds,
(*d*) „ „ „ „ padded Chrome colours,
(*e*) „ „ „ under printed covers and pads,
(*f*) Fast Indigosol discharges on silk dyed with Acid and Direct dyestuffs,
(*g*) Indigosol-padded grounds reserved by Chrome colours,
(*h*) „ „ „ „ Rapid Fast colours,
(*i*) „ „ „ „ printed naphthols,
(*j*) „ „ „ „ printed vat colours,

and, of course, the direct printed styles already dealt with in the preceding pages.

As these styles are closely associated, in their production, with the application of colouring matters and processes not yet dealt with, their description is deferred to sections 3, 4, and 5, treating of Insoluble Azoic Colours and Discharge and Resist Styles, respectively.

Apart from direct printing, the vat colours in general lend themselves admirably to the production of *resist* and *discharge* styles, and many of them also, particularly the members of the Indigoid group, are also capable of being perfectly discharged by the Leucotrope process. These styles will be dealt with under Resists and Discharges.

Unfortunately there is one great disadvantage attached to the use of the vat colours for general work, namely, that of expense. With regard to Ciba blues and other brominated Indigos, attention should be drawn to the fact that they are tinctorially weak, *i.e.* that in consequence of their great molecular weight a larger amount of dyestuff is required to produce a given depth of shade than is the case with such colours as Indigo. The high cost of these colours is not only due to their tinctorial weakness, but also to the large percentage of bromine which they contain. Indigo M.L.B./6 B., for instance, is the penta-brom compound of Indigo, and contains, therefore, about 60 per cent. of bromine, which is not merely an expensive substance itself, but is also the direct cause of the decrease in tinctorial value. With respect to other vat colours, the high price may equally well be attributed to the high cost of manufacture. For this reason alone the use of vat dyestuffs is restricted to the highest class of work in shirtings, dress, and certain furnishing materials, or such as are printed in pale shades.

It is to be hoped that in the near future the price of these excellent colours will be brought down to a point that will enable calico printers to apply them to a much wider range of styles than commercial considerations warrant them in doing at present.

The Sulphur Colours.

The dyestuffs known under the name of Sulphur colours are for the most part prepared by heating various organic bodies with sulphur, alone or along with sodium sulphide. In a sense they may be regarded as vat dyes, though they differ considerably from this group both in composition and constitution. Their constitution, in fact, has not yet been definitely ascertained, and their mode of preparation is entirely different from that of the typical vat dyestuffs.

At the same time they form leuco compounds like Indigo, etc., and may be applied in practically the same way, so that from a colourist's point of view they fall into the same class.

Of the vast number of Sulphur colours manufactured by different firms, the most important are those belonging to the Immedial, Thionol, Thional, Thiogene, Katigen, Kryogene, Pyrogene, Cross-dye, Thioxine, Eclipse, Rexoll, and Thionine series. The black dyestuffs of these series possess special interest for the reason that they give, either by printing or dyeing, a full black equally as fast as Aniline black to soaping and light, and free from the defect of greening when exposed to town atmospheres containing sulphur dioxide.

The greatest drawback of the Sulphur colours is that they blacken the printing rollers. This blackening is due to the presence of polysulphides which injuriously attack the rollers, with the formation of copper sulphide. To some extent this defect can be overcome by the addition of sodium sulphite or bisulphite to the alkaline printing pastes, but in this case the use of the hydrosulphites is inadmissible, since the final result of the reactions between the sulphite or bisulphite, the hydrosulphite, and the polysulphides or free sulphur in the colouring matter would be that the polysulphides would remain practically unaffected.

Within recent years many of the Sulphur dyestuffs have been more or less freed from free sulphur and polysulphides, and consequently they do not affect the printing rollers injuriously. Of these improved products, the Immedial colours soluble, and the D. brands of the Thiogene series, are typical examples. Some of these pure colours yield the best results with pure hydrosulphite of soda in powder, while others are preferably printed with sulphoxylate-formaldehyde compounds like Formosul, Britulite, Hydrosulphite A.F.C., etc. The latter compounds yield the most stable colours, but the stability of those prepared with the hydrosulphite in powder ($Na_2S_2O_4$) is sufficiently good for most purposes.

The printing of Sulphur colours must be carefully carried out. Their fixation depends to a great extent on the presence of plenty of moisture ; and in printing, therefore, it is essential to guard against overdrying the goods. In a great measure this is prevented by the addition of glycerine to the printing pastes, but it is well not to depend too much on the action of glycerine. The safest plan is to dry the goods in moderately hot air, and not over cylinders, if it can be avoided. A little China clay is often added to the printing colours to lessen their liability to run during the subsequent steaming in damp steam.

The preparation of the printing pastes is as follows :—

The colouring matter is beaten up with water, caustic soda, glycerine, China clay, and either glucose or one of the sulphoxylates already mentioned. The mixture is heated until the colouring matter is completely reduced and dissolved, and then added to the necessary quantity of alkaline thickening ; finally, the whole is warmed again until a perfectly homogeneous paste is obtained, which after cooling is ready for use. For very light shades it is possible to reduce the quantity of alkali down to an amount just necessary for the solution of the colouring matter, but, as a rule, it is better to keep the colours strongly alkaline.

The following recipes will serve as types of the general methods of preparing Sulphur printing colours:—

Black.

80	grms.	Thiogene black M.D. conc.
50	,,	glycerine.
150	,,	caustic soda 25° Tw.
80	,,	50 per cent. China clay paste.
40	,,	Formosul.
600	,,	alkaline thickening (for Indigo).
1000		

Light Blue.

10	grms.	Thiogene cyanine C.D. extra.
30	,,	glycerine.
30	,,	caustic soda 25° Tw.
150	,,	water.
150	,,	China clay paste 50 per cent.
20	,,	Formosul.
610	,,	alkaline thickening 2 : 1.
1000		

Green :—as blue, but Thiogene green C.L.F. extra conc.

Yellow :— ,, ,, ,, yellow.

Grey :— ,, ,, ,, grey B.D. extra conc.

Dark Blue.

25	grms.	Thiogene cyanine O.D. extra.
50	,,	glycerine.
150	,,	caustic soda 25° Tw.
100	,,	50 per cent. China clay paste.
20	,,	Formosul.
600	,,	alkaline thickening for Indigo.
55	,,	30 per cent. gum Senegal mucilage.
1000		

Other methods of printing Sulphur colours, in current use, are based on the reducing action of glucose and sodium sulphide in the presence of caustic soda ; but, as better methods are now available, they are rapidly falling into disuse in progressive works. The two following examples will suffice to illustrate the preparation of the printing colours :—

With Sodium Sulphide.

20	grms.	Sulphur colour (dry).
140	,,	boiling water.
50	,,	fused sodium sulphide.
10	,,	glycerine.
25	,,	soda-ash (or caustic soda 60° Tw).

Dissolve and add :—

745 grms. British gum 1 : 1 solution.
5 ,, oleine 40 per cent.
5 ,, turpentine.

1000

Heat to 140° F. and cool.

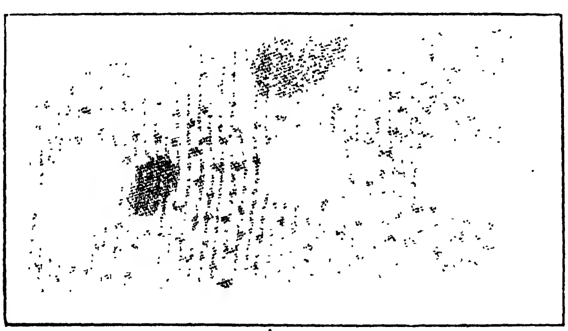
WITH GLUCOSE.

40	grms.	Sulphur colour (dry).
40	,,	caustic soda 60° Tw.
25	,,	glycerine.
100	,,	water.
425	,,	alkaline thickening (as for Indigo).
320	,,	British gum 1 : 1.
25	,,	glucose syrup.

Heat to 140° F., cool, and add—
25 grms. glucose 1 : 1.

1000

It has been already pointed out that the chief disadvantage of Sulphur colours printed by ordinary methods is that they attack the printing rollers (and also the " doctors ") owing to the fact that they contain, in one form or another, active polysulphides. The effect of the latter in blackening and corroding the rollers and " doctors " can be prevented entirely by the addition of 0·5–1 per cent. potassium cyanide—an efficient but somewhat risky device to which resort ought not to be made except under strict supervision. Another and safe means of attaining the same end is described by B. J. Cheshire in the "*Pli cacheté* 2010" and was recently published by the Industrial Society of Mulhouse.[1] In this process sodium sulphide as such, and all other reducing agents, are replaced by a condensation product of sodium sulphide with formaldehyde-bisulphite. On steaming, the condensation product dissociates and the Sulphur dyestuff, in the presence of alkali, is reduced on the fibre. Printing colours made-up in accordance with the following recipes neither attack the rollers nor destroy the edge of the cleaning " doctor."



Thional Yellow G. Conc. (Sandoz).

[1] "*Pli cacheté No.* 2010," July 2nd, 1910; *Bull. Soc. Ind. Mulhouse*, 1932, pp. 555–558.

YELLOW.

50	grms.	Thional yellow G. conc.
60	,,	glycerine.
40	,,	caustic soda 67° Tw.

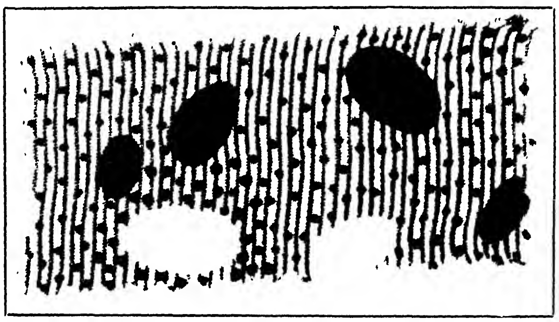
Mix to a fine paste and add—

150 c.c. water.
400 grms. British gum 1 : 1.

Heat until dissolved ; cool to 100° F., and add—

300 grms. condensation product S.F.B.

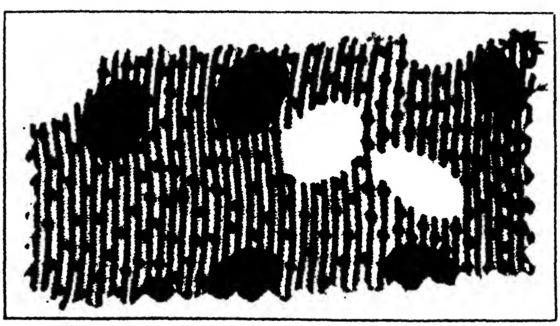
1000



Thional Red Violet R. Conc. (Sandoz).

VIOLET.

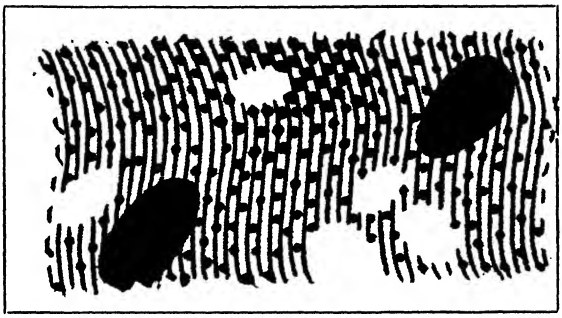
11	grms.	Thional red violet R. conc.
60	,,	glycerine.
40	,,	caustic soda 67° Tw.
89	,,	water.
500	,,	British gum 1 : 1.
300	,,	condensation product S.F.B.
1000		



Thional Brilliant Blue G. Conc. (Sandoz).

Blue.

25	grms.	Thional brilliant blue G. conc.
60	,,	glycerine.
40	,,	caustic soda 67° Tw.
175	,,	water.
400	,,	British gum 1 : 1.
300	,,	condensation product S.F.B.
1000		



Thional Brilliant Green 3 G. Conc. (Sandoz).

Green.

30	grms.	Thional brilliant green 3 G. conc.
60	,,	glycerine.
40	,,	caustic soda 67° Tw.
170	,,	water.
400	,,	British gum 1 : 1.
300	,,	condensation product S.F.B.
1000		

The initial pasting of the dyestuff with glycerine is facilitated by a small addition of Tetracarnit.

Condensation Product S.F.B.

2000 grms. formaldehyde 40 per cent.
1000 ,, sodium bisulphite 67° Tw.

Mix and add gradually—

1000 grms. sodium sulphide (calcined).

Stir at intervals, allow to stand and react for 24 hours. The resulting grey paste is used as described.

The white oval objects in these patterns have been produced subsequently by blocking-in a discharge white.

Other series of Sulphur colours are applied according to one or other of the foregoing formulæ.

After drying, all goods printed with Sulphur colours are passed once or twice through moist steam at 102° C. The steaming takes place in the rapid ager, and lasts from 3–5 minutes according to circumstances. The goods may then be passed through one of the solutions given below:—

	1.	2.	3.	
Water	1000	1000	1000	grms.
Sulphuric acid 168° Tw.	10	10	10	,,
Copper sulphate	..	2	..	,,
Bichromate of potash	..	..	5	,,

Finally, they are well washed and soaped.

As a rule recipes of the above types, containing a large proportion of caustic soda, are essential to the production of the deepest shades. For light shades the proportion may be reduced with advantage, and with a few colours even dark shades may be obtained by discarding caustic soda entirely in favour of soda-ash or potash. In this connection Immedial green G.G., Immedial Indone violet, and Thional brilliant green G.G. are the most important. In the case of the Thional series a bisulphite process has been recommended in which the alkali is, more or less, neutralised.

The two following recipes will serve to illustrate the preparation of printing colours by these methods:—

Carbonate Process.

100 grms. Immedial brilliant green G.G.
60 ,, glycerin.
800 ,, K.C. paste (see Ciba blue).
20 ,, hydrosulphite conc. ($Na_2S_2O_4$).
Heat to 140° F., and add—
20 grms. Formosul.

1000

Bisulphite Process.[1]

20 grms. Thional brown B.
80 ,, boiling water.
20 ,, bisulphite of soda 66° Tw.
500 ,, British gum thickening, 50 per cent.
300 ,, gum arabic, 50 per cent.
40 ,, caustic soda 76° Tw.
40 ,, water.

1000

After printing, steam, etc., as for other methods.

Sulphur colours are employed mainly in the direct printing of shirtings, and other goods, that are required to stand the action of light and frequent washing without the necessity of also resisting chlorine. For a long time after their first introduction into commerce their use was restricted to dyeing only; the earlier colours were too impure, contained too much sulphur and

[1] G. Tagliani.

sulphide, and were too insoluble for printing purposes. They also contained a great deal of gritty matter which rendered them almost impossible to strain, and this, in conjunction with the above defects, caused them to give unsatisfactory results, both as regards regularity of shade and the working quality of the printing pastes. With improved methods of manufacture, however, there is now available a great variety of fast and fairly bright colours, and the printing of the new and soluble products has rapidly developed into an important branch of manufacture.

The colours purified specially for printing work well, do not stain the rollers to any great extent, require only a short steaming for their fixation, and yield sufficiently bright colours of excellent fastness to washing. Moreover, they are easily reserved, and are therefore of great value in the *print and cover style* for the production of direct printed effects that formerly could only be obtained, of equal fastness, by the tedious method of dyeing on a previously printed, aged, and fixed mordant.

The Sulphur colours will stand a much larger quantity of hydrosulphite than is required for their reduction, and this allows of their being used as discharge colours on Paranitraniline red and other Insoluble azoic colours, and also on direct dyestuffs. They are not very bright colours, but for quiet effects on flannelettes, and in all cases where fastness is required, they are exceedingly useful. For combined brightness, fullness, and fastness, nothing has hitherto surpassed the vat dyestuffs; but the Sulphur colours are none the less useful for a great variety of styles, and they include a greater range of quiet shades than any other series of vat dyestuffs.

In common with the Ciba colours, Indanthrenes, and Indigo, they can be printed on naphthol-prepared cloth in conjunction with any Insoluble azoic colour. They are also dischargeable by the chlorate prussiate method; and as they are easily reserved by zinc salts and Leucotropes, they are applicable to a great variety of styles.

With very few exceptions, the Sulphur colours are sensitive to chlorine, but in other respects they represent one of the fastest classes of colours known. It must, however, not be taken for granted that a Sulphur colour is necessarily fast. There are, in fact, some which could not even be termed moderately fast.

The *reserving* and *discharging* of Sulphur colours will be dealt with in another section of this work.

It is impossible to review, or even to mention, all the many excellent Sulphur colours on the market. As a class they are very similar; they are all applied according to the principles illustrated in the foregoing examples of printing pastes, and in general they behave in much the same way as the colours mentioned above.

Steam Mineral Colours.

With the single exception of Prussian blue, the production of mineral pigments on the fibre by steaming is a thing of the past. The shades so obtained are neither so bright nor, of necessity, so intense as those got by first printing a salt of one of the main constituents, and then precipitating the pigment by running through a bath containing the other constituent.

Steam Chrome Yellows and Oranges may be obtained, according to H. Schmid, by printing a mixture of a soluble lead salt and an insoluble chromate.

A suitable recipe for the preparation of steam chrome yellow is as follows:—

STEAM CHROME YELLOW.

400 grms.	6 per cent. gum tragacanth thickening.	
70 ,,	acetic acid 9° Tw.	
110 ,,	lead nitrate	or 250 of lead acetate.
120 ,,	lead acetate	

Dissolve and add, when cooled a little,

100 grms.	aluminium nitrate-acetate 28° Tw. Cool and add—
200 ,,	zinc chromate 50 per cent. (or 170 grms. of barium chromate 50 per cent.).
1000	

Print, steam for one hour, pass through a hot bath of—

25 grms.	sodium sulphate	at 140° F.
0·5 ,,	tartaric acid	
1 litre water		

Wash and dry.

The above gives a lemon-yellow pigment of a composition approximating to $PbCrO_4.PbSO_4$. It also contains a little aluminium oxide, which, as is well known, tends to preserve the delicate tone of lemon chrome. The small quantity of tartaric acid in the sodium sulphate solution ensures the absence of any free carbonates, which would, of course, be liable to redden the shade of the yellow. At the same time, it probably reduces a minute portion of the chromate, thus helping to preserve the greenish canary yellow of the finest shades of lemon yellow.

A chrome orange proper cannot be obtained by steaming alone, but a much redder shade of yellow, which can afterwards be converted into a pure orange, can be obtained by a modification of the above recipe for the lemon yellow.

STEAM CHROME ORANGE.

200 grms.	lead nitrate.
435 ,,	5 per cent. tragacanth thickening.

Dissolve and add when at 80° F.—

25 grms.	acetate of soda.
340 ,,	barium chromate 50 per cent. paste.
1000	

Print, steam, and soap.

This printing colour gives a golden or maize yellow, which (if printed with colours that will stand the treatment) may be converted into an orange by passing through boiling lime water (1/1000, or 1 lb. quicklime in 100 gallons of water). When six " lumps " of 120 yards each have passed through, the bath is replenished with 175 grms. of lime per 1000 litres, or 2½ oz. per 100 gallons. After " liming," the goods are well washed and soaped.

The great defect of all lead yellows is that they tend to blacken when exposed to the impure air of towns. This is due to the formation of lead sulphide caused by the presence of sulphuretted hydrogen in the atmosphere.

Cadmium Yellow, on the contrary, is a sulphide itself, so that it is quite unaffected by sulphuretted hydrogen. In fact, the chief use of cadmium salts in calico printing is not for the production of the fine but expensive pigment so largely used by artists, but for the preservation of precipitated lead yellows. For this purpose a certain amount of cadmium nitrate is ground up and dissolved in the pigment paste; and so long as any soluble salt of cadmium remains, the sulphuretted hydrogen will combine with it in preference to acting upon the insoluble and more inert lead chromate.

In cases where its expense is not prohibitive, cadmium nitrate may be used for the production of an exceedingly brilliant yellow, which is quite permanent in impure atmospheres, and quite as fast to light and soaping as the various lead yellows. The formation of cadmium sulphide on the fibre by steaming depends upon the action of sodium thiosulphate on a soluble cadmium salt. Whether free sulphur is liberated during the reaction in the steaming chamber, or whether an unstable cadmium thiosulphate is the first product, is not definitely known. The latter explanation is perhaps the more likely, though it is possible to obtain the same result by steaming a mixture of flowers of sulphur and cadmium nitrate.

$$(1)\ Cd(NO_3)_2 + Na_2S_2O_3 = CdS_2O_3 + 2NaNO_3.$$
$$(2)\ CdS_2O_3 + H_2O \underset{\text{Steam.}}{=} CdS + H_2SO_4.$$

In any case free mineral acid is liberated, as is proved by the tendering of the fibre. This latter defect is overcome by the addition of sodium acetate. The final result may perhaps be expressed by the following equation:—

$$Cd(NO_3)_2+Na_2S_2O_3+H_2O+2NaC_2H_3O_2=CdS+2NaNO_3+Na_2SO_4+2C_2H_4O_2.$$

The recipe given below is based on these lines, and was formerly in use on the large scale.

STEAM CADMIUM YELLOW.

100 grms. cadmium nitrate.
670 „ 5 per cent. tragacanth thickening.

Dissolve, cool, and add—

110 grms. sodium thiosulphate.
120 „ sodium acetate.

1000

Allow to stand a day or two before use. Then print on white cloth, steam for an hour, wash, and soap.

As a printing colour, Cadmium yellow, in spite of its excellent qualities, has never been employed to anything like the same extent as the lead chromates; and this not merely on account of its greater cost, but because, for most purposes, the chrome yellows and oranges are sufficiently permanent, and at the same time adaptable to a greater variety of styles.

Prussian Blue.—Prior to the introduction of the aniline colours, Prussian blue was the only really bright blue at the disposal of the calico printer. The usual method of obtaining blue patterns was to pass cloth mordanted (by printing or padding) with ferric oxide through an acidulated solution of potassium ferrocyanide.

$$4Fe(OH)_3 + 3K_4Fe(CN)_6 + 6H_2SO_4 = \underset{\text{Prussian blue.}}{Fe_4[Fe(CN)_6]_3} + 6K_2SO_4 + 12H_2O.$$

The presence of tin salts imparts a fine purplish tone to the blue, and in all steam Prussian blues stannous ferrocyanide plays an important part. Other ingredients also are added to assist the reaction during the steaming operation, *e.g.* mineral acids which liberate the hydroferri- or hydroferrocyanic acids which decompose under the influence of steam with the formation of insoluble Prussian blue, and organic acids which act as solvents (oxalic), and generally accelerate the production of the blue.

Steam Prussian blues consist essentially of stannous and potassium ferrocyanides and acids or acid salts. Most of them, however, contain ferrocyanide

of potash in addition to the other ingredients, and its presence undoubtedly improves the shade. After printing, they are steamed, and then passed through a warm chrome bath, or a very weak solution of bleaching powder, to ensure the complete oxidation of any ferrous ferrocyanide which may have escaped oxidation during steaming.

An exposure to the air for some time would have the same effect, but chroming develops the colour instantaneously, and is, moreover, a necessary operation in the production of styles to which Prussian blue is well adapted.

The preparation of printing colours was formerly a matter of profound secrecy among colour mixers, and, as a result of their rule of thumb methods, the proportions of the ingredients employed to obtain one and the same effect differed considerably. Each colour mixer worked according to his fancy, hence the existence of a large number of recipes for steam Prussian blue, which was formerly the only bright blue available, and, as such, one of the most important colours then known.

It would serve no useful purpose to give a selection of these old recipes; many of them are badly balanced, and most of them are better fitted for Turkey-red discharging than for steam work; they contain an unnecessarily large excess of acid, and, judging from practical trials of a few of them, they must have caused an immense amount of damage in the way of tendering the cloth.

The following two recipes have given good results in general steam work on the large scale, and will serve as types of the preparation of steam Prussian blue:—

Steam Prussian Blue I.

350	grms.	water.
70	,,	starch.
10	,,	ammonium chloride.
15	,,	olive oil. Boil, cool, and add—
400	,,	tin pulp 30 per cent.
60	,,	yellow prussiate of potash (finely ground).
30	,,	red ,, ,, ,,
30	,,	tartaric acid (powdered).
5	,,	oxalic acid.
25	,,	water.
5	,,	sulphuric acid 168° Tw.
100	,,	water.
1100 = 1000 after boiling the first part.		

Steam Prussian Blue II.

300	grms.	water.
120	,,	light British gum.
60	,,	yellow Prussiate of potash.
40	,,	ammonium chloride. Boil, cool, and add—
400	,,	tin pulp 30 per cent.
20	,,	red prussiate.
60	,,	boiling water.
10	,,	alum (finely ground).
20	,,	bisulphate of soda [$NaHSO_4$] (powdered).
5	,,	oxalic acid.
5	,,	sulphuric acid 168° Tw.
60	,,	water.
1100 = 1000 when finished.		

Print both these blues on either oiled or unoiled cloth; steam the goods for an hour, and then develop the full shade by a short run through a ½ per cent. solution of bichromate of potash at 140° F., wash well, and dry.

TIN PULP for foregoing recipes.

a { 430 grms. yellow prussiate of potash.
2000 ,, water. }

b { 450 ,, stannous chloride.
100 ,, hydrochloric acid.
2000 ,, water. }

Dissolve *a* and *b* separately; add them together; wash the precipitate 4–5 times by decantation, and then filter it to 1500 grms. = about 30 per cent. paste of tin ferrocyanide.

In addition to acting as a simple blue, Prussian blue was also employed as the blue element of fast, deep steam greens. For this purpose it was combined with Persian berry or Quercitron bark extracts, the tin lakes of which are very bright; so that very good clear greens and olives resulted from the mixture.

STEAM PRUSSIATE GREEN I.

520 grms. water.
140 ,, Persian berry extract 48° Tw.
65 ,, powdered alum.
145 ,, British gum.
100 ,, yellow prussiate of potash.

Boil, cool, and add—

{ 15 grms. stannous chloride.
15 ,, oxalic acid.
110 ,, water. }

1110 = 1000 when finished.

STEAM GREEN II.

530 grms. water.
140 ,, Quercitron bark extract 48° Tw.
60 ,, alum.
145 ,, British gum.

Boil, cool a little, and add—

100 grms. tin ferrocyanide (tin pulp), 30 per cent.
{ 10 ,, red prussiate of potash.
50 ,, boiling water. }
{ 15 ,, oxalic acid.
50 ,, boiling water. }

1100 = 1000 when finished.

Print, etc., exactly as for Prussian blue.

The chief drawback of all Prussian blues is that they will not stand soaping. The slightest excess of alkali decomposes them, leaving yellow ferric oxide on the fibre. Exposure for any length of time to strong light causes them to fade somewhat, but they recover their original intensity again if kept in a dark place.

Steam Manganese Brown.—The excellent fastness of Manganese brown or Manganese bronze produced as a plain shade by passing cloth padded in manganese chloride through a solution of caustic soda and bleaching powder, or bichromate of potash and ammonia, led to several attempts being made to

obtain the same colour directly by printing and steaming. Of these, the most successful was the method suggested by Balanche, who printed a mixture of manganese chloride, bichromate of soda, and acetate of soda. On steaming, an unstable chromate of manganese is formed which decomposes, with the ultimate formation of the brown oxide. The acetate of soda is added to prevent the tendering of the fibre by the hydrochloric acid liberated during the reaction.

Steam Manganese brown is out of date at the present time, having been displaced by other and more generally applicable colours. The following recipe will serve to illustrate the method of Balanche.

STEAM MANGANESE BROWN.

500 grms. water.
10 ,, olive oil.
100 ,, starch.

Boil, turn off steam, and, when cooled a little, add—

150 grms. bichromate of soda.

Cool and add—

125 ,, manganese chloride [$MnCl_2.4H_2O$].
125 ,, acetate of soda.

1010=1000 after boiling first part.

Print, steam, allow to lie an hour or two, and then wash and soap. If the other colours of the design allow of it, the goods are improved by a short run through a solution of bleaching powder ½° Tw. immediately after steaming, in which case they may be washed and soaped at once without the necessity for lying exposed to the air.

All the steam mineral colours may be used in combination with the vegetable yellows and browns, and with a strong Logwood-iron or Logwood-chrome black; but the styles of work for which they were formerly in demand are now executed by other and more reliable means, and they have fallen into practically complete disuse.

The Loose Steam Style.

This style is characterised by the brilliancy and fugitiveness of its colours. Any colouring matter that will give the required shade is used irrespective of its fastness or its capability of being fixed upon the fibre. The goods are not required to undergo any washing, fixing, or soaping operations, and are ready for finishing as soon as they are steamed. Even steaming is dispensed with, except in cases where it is cheaper or more convenient to use a mordant colour —*e.g.* Logwood black, Alizarin chocolate, Persian berry yellow, etc.—than to make up a special loose colour.

The cloth is usually prepared in oleine, as already described, and the goods, after printing and steaming, are finished at once either by back starching or simply by hot calendering.

Alizarin is often used for the red in loose work, and the olives and browns, blacks and chocolates are, as a rule, fast mordant colours, simply because they are the cheapest; but the pinks are for the most part phthaleïn colours like Phloxine, Eosine, and Rose Bengale; the yellows Auramine or Thioflavine T. without tannic acid; and the blues, violets, greens, and oranges are also basic colours without any mordant whatsoever. The basic aniline colours printed on oiled cloth are exceedingly bright, and are to some extent fixed, but they cannot be regarded as fast colours when so applied; in fact they are very loose to soap, and much less permanent to light than when fixed as double tannates.

Most of the acid colours are also largely employed in the loose steam style, either alone or in conjunction with alumina or chrome mordants, with which they form lakes that are just sufficiently insoluble to prevent the colours from running during the processes connected with finishing. They are quite loose to soap.

The Croceïn scarlets and various other acid reds, none of which can be fixed on cotton, are all used for red grounds in loose work on calico. They produce excessively brilliant fiery reds, that wash out almost completely on soaping. In short, any colour that will yield the desired effect may be used in loose work, whether it be fast or loose, a dyestuff proper, or merely a stain. Dark colours like blacks, navy blues, and chocolates, also olives, are generally fast mordant colours, while the lighter and brighter pinks, yellows, greens, and blues are obtained either from the acid colours, phthaleïn colours, or basic colours simply thickened, with or without the addition of Alizarin oil, or the acetates of aluminium or chromium.

For Eosines and acid colours the following directions may be followed; the basic colours require no special mention:—

EOSINE PINK (with chrome).

25	grms.	Eosine or Erythrosine.
250	„	water.
650	„	starch or tragacanth paste.
75	„	acetate of chrome 30° Tw.
1000		

All Eosines, Phloxines, Erythrosines, Rose Bengale, Uranine yellow, and other phthaleïn colours may be made up according to this recipe. If desired, the chrome may be left out, but the colours are apt to run in finishing if no chromium salt is present.

CROCEÏN SCARLET (with alumina).

35	grms.	Croceïn scarlet (any brand).
350	„	water.
515	„	tragacanth, 5 per cent.
100	„	acetate of alumina 25° Tw.
1000		

This recipe will serve for all brands of oxy-azo colours of the Croceïn class; also for Naphthol yellows, etc., for which alum may be used in place of acetate of alumina.

The Soluble and Alkali blues may be applied in much the same way.

SOLUBLE BLUE.

35	grms.	Alkali or Soluble blue.
300	„	water.
50	„	ammonium citrate 20° Tw.
50	„	neutral Turkey-red oil.
515	„	starch-tragacanth paste.
50	„	acetate of chrome 30°.
1000		

All the ammonium and sodium salts of the Rosaniline blue sulphonic acids can be applied in the same way.

The loose steam style of printing is used mainly for temporary decorations,

and for certain foreign markets where brilliancy and cheapness are more important than fastness. Commercially it may be of some value, but technically and artistically it is of no interest whatever. The designs employed are frequently of the highest class, being those that have already served their purpose in previous years for the home market, but the colours in which they are printed are for the most part outrageously crude and vulgar; and while, perhaps, harmonising well enough with the brilliant surroundings of the East and the Tropics, they are at the same time unsuited to those regions by reason of their general fugitiveness.

Padding and Covering Styles.

These styles are not restricted to any particular class of colouring matters, and therefore they may be described here as well as elsewhere. In fact the effects obtained by *padding* and *covering* are due more to the mechanical means of applying the colouring matters to the fibre than to the chemical operations concerned in their fixation.

A padded or covered print displays a pattern, either in white or colour, or both combined, on a plain or figured coloured ground; and differs from an ordinary multicolour print, not in appearance, but in the method of its production, which allows of the same ground roller being used for any number of patterns. These patterns may be printed at separate times, and then all be covered or padded at once with one roller, thus effecting a great saving in both engraving and material (copper).

A cover roller is a copper roller engraved *all over* its surface with a fine delicate pattern, such as, for instance, a fine check, a honeycomb, a continuous trail, a series of fine perpendicular or of oblique lines or spots, etc.; and a pad is a roller engraved so as to print an uniform flat tint over the whole of the cloth, *i.e.* dye it on one side only. It is obvious that if a lighter colour is printed, with either of these rollers, on cloth already printed in a darker pattern, the latter will show through the lighter ground, and its darker colour will mask the paler tint of the over-print. When a white pattern is required on a coloured ground obtained in this way, the cloth is first printed with a mixture containing some substance or substances, capable of preventing the fixation of the colour applied by the cover or pad roller. These mixtures are known as *resists* or *reserves*, and they act in various ways, sometimes destroying the colouring matter, sometimes preventing its combination with the mordant, and sometimes forming a soluble and stable compound with the mordant, which is washed out of the cloth in subsequent operations. Apart from their chemical action, resists also act mechanically by obstructing the entrance of the colour into the body of the cloth to be printed. Occasionally, indeed, their action is entirely mechanical.

The composition, etc., of the numerous resists used for different classes of colouring matters and mordants will be dealt with in a special chapter. It may be noted here, however, that citric acid, citrates or tartrate of chromium are the resists most commonly employed for Alizarin pinks.

The *modus operandi* in producing a red and white pattern on a pink or red ground by steaming is as follows:—

(1) First print, on oiled cloth, a two-colour design in steam Alizarin red and a thickened solution of tartrate of chromium. Dry the goods well and then—

(2) Over-print them with either a cover or pad roller in steam Alizarin red or pink. Dry well.

(3) Steam for one hour in the continuous steamer, wash well, and soap.

Wherever the tartrate of chromium has been printed, the ground colour

printed over it will have been prevented from developing during the steaming operation, and in the final washing and soaping it will be removed entirely, carrying along with it those portions of the undeveloped colour which fell over it in the second printing, and leaving a more or less perfectly white object in its place. The red is, of course, unaffected by the over-printing, and develops in the usual way; so that the final effect obtained is that of a red and white pattern on a pink ground. The ground will be plain or patterned according as the roller used in the second- or over-printing was a pad or a cover. A red pattern will, if large enough, show up well on a fine red *cover*, but it is almost needless to point out that a *pad* should always be lighter than the lightest colour in the pattern to be padded.

By employing suitable resisting agents, similar effects to the above can be obtained with the Insoluble azoic colours, Sulphur colours, basic aniline colours, Aniline black, iron and aluminium mordants (dyed style), and, in fact, with almost every group of colouring substances known.

The object of both resisting and discharging processes is the same, *i.e.* the production of a white or coloured design on a coloured ground that has not been specially engraved for it. The main difference between the two, apart from chemical questions, is that in the case of resists the development or fixation of the ground colour is prevented altogether, while in the case of discharges the fully developed ground colour is subsequently destroyed by the oxidising or reducing action of the discharging agents—in a word, bleached out.

Colours produced on the Fibre by Condensation.

In the year 1898 the Farbwerke Höchst patented a process for the direct production and simultaneous fixation of certain basic colours on the fibre.

These colours are obtained by the condensation of the nitroso-bases of tertiary aromatic amines with various phenols, and constitute what are known as the oxazine dyestuffs. They form insoluble lakes with tannic acid, and their mode of application allows of all the components of the lakes being printed on the cloth together and without any previous preparation. A short steaming in the rapid ager is sufficient to develop the colour, which is then further fixed, in the usual way for basic dyestuffs, by a run through tartar emetic.

Several nitroso-bases and several phenols may be used in the production of these colouring matters, but the most interesting, and in fact the only, combination used to any extent on the large scale is Resorcin blue M.R., the result of the condensation of p-nitroso-dimethylaniline with resorcin.

The other bases and phenols yield different shades of blue, which have been distinguished from the above by the brand marks Resorcin or Nitroso-blue A.D., M.D., T.O., etc. They are not in much demand, as the Resorcin blue M.R. gives the most popular shade of navy blue.

Although the Nitroso- or Resorcin-blues are useful for the direct printing of dark navy-blue blotches, their most important application is in the production of imitation Indigo discharges. For this purpose the cloth is slop-padded in a mangle through a solution of the blue mixture; and as the development of the colour is prevented entirely by the presence of reducing agents, it is easily possible, by printing these on the padded and dried cloth, *before steaming*, to obtain fine resist effects in white and colours on a deep indigo-like ground.

Para-nitroso-dimethylaniline comes into commerce either solid or in the form of a 50 per cent. paste, as Nitroso-base M.; and resorcin is supplied either as such, or mixed with the requisite quantity of tannic acid, as Tannoxyphenol R. The hydrochloride of p-nitroso-dimethylaniline may also be used

in place of Nitroso-base M.; it is very soluble in water, but otherwise has no advantage over the base.

In preparing either the printing or the padding colour the following directions are to be observed:—

The nitroso-base is first dissolved in water containing hydrochloric acid and a little glycerin, and is then mixed with the thickening; to this is added a solution of resorcin or Tannoxyphenol R. in water, and finally a small quantity of oxalic acid. If resorcin is used, the tannic acid is added separately, and either before or after the oxalic acid.

Nitroso-Blue M.R. (for printing), (M., L. & B.) I.

	6,000 grms.	acid starch paste.
	200 ,,	glycerin.
Add—		
	260 ,,	Nitroso-base M. 50 per cent.
	207 ,,	water.
	87 ,,	hydrochloric acid 36° Tw.
Mix well and add—		
	200 grms.	resorcin in
	1,470 ,,	water.
	60 ,,	oxalic acid.
	500 ,,	water.
	600 ,,	tannic acid 50 per cent. solution in acetic acid.
	400 ,,	phosphate of soda 20 per cent. solution.
	To 10,000 ,,	with water.

Print on white cloth, dry gently, steam for 2–3 minutes at 212° F. in the rapid ager, and then fix through tartar emetic exactly as for basic dyestuffs, wash and soap.

With Tannoxyphenol the same procedure is observed, except that the above quantities of resorcin and tannic acid are replaced by 325 grms. of Tannoxyphenol.

The phosphate of soda is introduced to prevent the tendering of the fibre by the acids during steaming.

The amount of tannic used has considerable influence on the shade produced. By diminishing the above quantity a redder and rather darker shade of blue is obtained; by increasing it, the shade becomes greener and a little lighter, and at the same time faster to soaping.

Padding colours are made up in exactly the same way as printing colours, with the exception that the acid starch paste is replaced by water or a thin tragacanth mucilage.

For particulars of the methods of resisting Nitroso-blues, see under "Resists and Discharges."

The drying of Nitroso-blues, whether printed or padded, requires careful attention. If possible, the goods should be dried in hot air, care being taken to prevent them from touching any of the drying chests that may form part of the apparatus. If over-dried, the final shade becomes dull and grey-looking. The best results are obtained when the colour of the dried goods is a pure bright yellow. At the same time, by working with an acid colour containing no phosphate, it is possible, with care, to dry the goods over steam-heated cylinders, and yet obtain satisfactory results. In such cases the first three or four cylinders must be wrapped with calico, and the temperature of the rest must be kept down to a point just sufficient to dry properly. The colour given below has given good results in practical trials.

RESORCIN BLUE II.

26	grms.	Nitroso-base M. 50 per cent.
25	,,	water.
20	,,	phosphoric acid 50 per cent.
633	,,	acid starch paste.
Mix and add—		
20	,,	resorcin.
150	,,	water.
30	,,	tannic acid.
30	,,	acetic acid.
6	,,	oxalic acid.
60	,,	water.
1000		

Print, dry gently as described, steam 2–3 minutes at 200° F., fix in tartar emetic and chalk, wash and soap.

Another colour which may be dried over cylinders is as follows:—

NITROSO-BLUE III.

530	grms.	thick starch-tragacanth paste.	
15	,,	glycerin.	
24	,,	Nitroso-blue base M. 50 per cent.	Dissolve lukewarm.
200	,,	acetic acid 9° Tw.	
Mix, cool, and add—			
20	grms.	resorcin in	
100	,,	water.	
60	,,	20 per cent. oxalic acid solution.	
60	,,	50 per cent. acetic acid tannin solution.	
Make to 1000			

Print, etc., as for Blue II.

Nitroso-blues, being fixed with tannic acid, can be toned at will by the addition of suitable basic dyestuffs, or they can be mixed with existing basic printing colours to produce greens, etc. The usual colours made use of for toning are Auramine, Methyl violet, Methylene blue, and Brilliant and Methylene greens.

Nitroso-blue M.R., when produced according to the first recipe, can be steamed for an hour, after the first short run through the rapid ager, without injuring the shade and without tendering the fibre; so that it is suitable for printing along with Alizarin red and other steam colours.

The Nitroso colours form a group apart from all others; but as they resemble steam colours more than any other class, and as they are applied by direct printing, they have been described along with this style in preference to treating them in a special chapter.

Notes on the Preparation of Compound Shades.

It rarely happens that all the separate colours of a multicolour pattern are obtained from pure unmixed dyestuffs. In the majority of cases, not more than one or two of the colours of an elaborate colour scheme are so obtained, the rest of them, consisting of various shades of brown, olive, gold, grey, etc., being produced by the admixture of two or more suitable colouring matters. Since by far the greater number of printing colours in everyday use consist of mixtures of this sort—compound shades that are impossible to obtain from

any single dyestuff—it is necessary that the calico printer's colourist should not only understand how to apply individual dyestuffs (that is, what thickenings, mordants, etc., to use), but that he should also know how to modify the shades they yield, and how to combine them for the production of the thousand and one soft, delicate, subdued colours that play so important a part in modern high-class textile printing. Merely to match or modify the actual shade of a colour is, at most, a question of a more or less lengthy series of experiments; but to match or modify it as desired, in the shortest possible time, and in such a manner that its component colours will all behave in, approximately, the same way towards light, soap, and other destructive agencies, requires some knowledge of the theory of colour, and of the properties of the colouring matters employed.

For all practical purposes, the Newtonian theory of colour, which takes red, yellow, and blue as the primary colours, orange, green, and violet or purple as the secondaries, and the various shades of brown, olive, grey, etc., as tertiaries, is the only one applied in textile colouring. But it must be regarded more as a technically valuable, and quite the most convenient, *system of colour mixing* rather than as a scientific *theory of colour*; for while it accounts satisfactorily for the effects obtained by the combination of *coloured bodies*, it was based upon an erroneous conception of the nature of colour itself, and consequently it breaks down when applied in explanation of many of the most striking colour phenomena observed by later workers in the field opened up by Newton's own discovery that white light is a compound of seven distinct colours.

The following definitions will make plain the meaning of some of the terms used to distinguish between the various qualities of colour, and in connection with colouring matters.

(1) Colour itself is a mental effect produced by the wave pressure of the "ether" on that ultra-sensitive portion of the optic nerve which constitutes the retina of the eye. The waves of undecomposed white light produce the sensation of white, hence colour is the intangible product of the decomposition of light.

(2) Colouring Matters, be they pigments, dyestuffs, or any other substance, are the material agents which decompose immaterial light in such a way that only one of its constituent colours, together with a larger amount of unaltered white light, is reflected from their surfaces. All bodies absorb a certain amount of light. If very little is absorbed, and that little as such, the body is white; but if the absorbed light be decomposed, the body appears coloured, and its particular colour depends upon which of the decomposition products it is unable to retain permanently. Thus a piece of Turkey-red cloth appears red in white light because, while reflecting the greater portion of the red light falling upon it, it absorbs the green rays, the rest complementing each other to form white light. But red is also capable of reflecting orange and purple, and if looked at through blue and yellow glasses will appear purple and orange respectively, owing to the fact that it reflects or returns just those particular shades of the two colours to which the glasses are transparent. The same applies to the various analogous effects obtained with other colours. At the same time it must be observed that, although all coloured bodies are capable of reflecting, or are transparent to, any one of a certain limited range of colours, they never, under any circumstances, reflect or transmit more than *one* colour at a time, and that colour varies with the kind of light thrown upon them: to put it in another way, the powers of absorption and reflection of coloured bodies vary with the light in which they are viewed. Red absorbs green entirely; therefore when Turkey red is viewed in green light

it appears black, since pure green light contains no colour that is reflected by red.

Colouring matters will be referred to as *colours* simply from this point onwards.

(3) SHADE.—Strictly speaking, this term refers to the chromatic composition of a colour. Thus Indigo, Prussian blue, and Alizarin blue represent different shades of blue. In a wider sense, "shade" is applied to distinguish between different intensities of the same colour, as, for example, dark and light shades of Indigo. This use of the term is perhaps incorrect, but it is difficult to describe the effects it represents otherwise, except by the use of the following term.

(4) TINT refers to that condition of a colour arising out of its dilution with water, paste, gum solution, or white. Its shade remains the same, but its intensity or depth is reduced. By a tint is generally understood a very pale colour.

(5) REDUCTION is a term used to denote both the thickening paste employed to reduce the intensity of a colour and the reduced colour itself. Thus starch paste is a "reduction," and a four-reduction of Alizarin pink means that one part of standard pink has been added to four parts of starch paste or other thickening.

(6) TONE is the effect produced on a colour by various influences which apparently modify its shade. A yellow spot on a red ground appears to be greener than the same spot on a blue ground; and again, a pink is always a pink in white light, whether the light be dull or bright, but it has a different appearance in each case. The colour remains the same, but its tone is modified.

(7) HARMONY OF ANALOGY is the effect of arranging a series of similar colours of different shades, strengths, and tints, as, for instance, the combination of yellows, browns, oranges, and chocolates.

(8) HARMONY OF CONTRAST, on the contrary, consists in the pleasing arrangement of different colours. Thus a floral design may be arranged to show a harmonious effect by using different colours for the flowers, leaves, stems, and background. For example, red, pink, yellow, and pale blue flowers, green or olive leaves, brown stems, and a dark blue background.

(9) PRIMARY COLOURS are pure, unmixed colours. In all that relates to textile colouring and the arts generally, the primary colours are red, yellow, and blue. In their purest form they cannot be obtained by any sort of chromatic combination of other colours.

(10) SECONDARY COLOURS.—Orange, green, and violet are the result of mixing two primaries in any proportions.

(11) TERTIARY COLOURS.—Browns, greys, and olives contain all three primaries in various proportions. Their qualitative composition (chromatically) is the same, their particular character being due to the predominance of one primary over the others. Tertiary colours result from the mixture of either the three primaries, or a primary and its complementary secondary, or from any two secondaries in any proportions.

(12) COMPLEMENTARY COLOURS.—Helmholtz and Maxwell regarded those colours as complementary which, when mixed together, produced *white light.* But as no mixture of coloured bodies can possibly yield white, this definition does not apply to dyestuffs, etc., and some other must therefore be found.

As all known colours consist of one or more of the three primaries—red, yellow, and blue—and as it is universally recognised that the presence of each of these (or their compounds) is absolutely essential to the perfect harmony of any colour scheme, it is clear that the absence of any one of them would create

a feeling of dissatisfaction. The eye naturally craves for the missing colour—for the completion of the primary triad. So much so is this the case that it is impossible to look for long at a pure primary colour or an inharmonious combination without fatiguing the eye, which becomes to some extent blinded by the strain of continually striving to complete the set of primary colours. In order to avoid this colour weariness, it is customary in examining, say, Turkey red, for the cloth looker to cast his eyes from time to time on some bright-green object, such as green paper. Green being a secondary colour, composed of blue and yellow, makes up the complement, or completes the set of primary colours, and so affords relief to the eye.

The simplest method of determining the complementary of a given colour is to gaze fixedly at a fairly large spot of it for a minute or two, and then to cast the eye on a piece of white paper, when there will appear on the blank paper a similar spot, but of a quite different colour. This colour is the complementary of the one first looked at. If one eye only is used in the first instance, the effect of the complementary colour is much more pronounced by winking rapidly, with each eye alternately, at the white paper. In this way the following colours are found to be complementary:—

Red	to	Bluish-green.
Blue	,,	Yellowish-orange.
Yellow	,,	Indigo blue (reddish).
Violet	,,	Greenish-yellow (lemon).
Green	,,	Yellowish-red (scarlet).
Sky-blue	,,	Full orange.

From this it will be seen that each of the three primary colours is complementary to the secondary colour formed by the mixture of the two remaining primaries. The yellow taken as a primary is of a slight greenish tinge, *e.g.* lemon-yellow.

Complementary colours may be described equally well as those which, when mixed together in certain proportions, produce neutral grey or black. To dull or "flatten" the shade of any colour, therefore, it suffices to add a little of its complementary; a small quantity of black is thereby produced, and the principal colour is modified accordingly.

On the other hand, if, instead of mixing two complementary colours together, they are placed side by side, they mutually enhance each other's brilliancy. This is due to the fact that it is impossible to look at any colour for long without the sensation of its complementary being excited on the retina. It follows, therefore, that each colour is seen in its own light (the light that it reflects best), which, of course, adds enormously to the brilliancy of its shade. Complementary colours juxtaposed in this way are said to be in full contrast. The most telling contrasts are naturally afforded by combinations of the primary colours with their complementary secondaries, but contrasts of a more subdued character also arise out of the analogous arrangements of secondary and tertiary colours. Thus—

Purple,	full	contrast	with Yellow,	subdued	contrast	with	Olive.
Orange,	,,	,,	,, Blue,	,,	,,	,,	Grey.
Green,	,,	,,	,, Red,	,,	,,	,,	Brown.

Many of the finest and most artistic products of calico printing are produced in harmonious combinations of quiet tertiary colours, with a few touches of the more brilliant primaries and secondaries added here and there to enrich the whole, and give life and interest to what might otherwise be a dull, depressing effect.

At the same time, it must not be supposed that harmony in colour is in any way dependent on the use of broken tertiary shades. Quite otherwise, in fact; for perfectly harmonious results can be secured in any combination, simple or complex, which contains the three primary colours in proper proportions. The only condition of perfect harmony is that they be balanced properly; and so long as this condition is fulfilled, it matters not whether they are present as primaries, secondaries, or tertiaries. Thus the following simple arrangements of—

(1) Red, Blue, and Yellow (brilliant),
(2) Orange, Purple, and Green (bright),
(3) Brown, Bluish-grey, and Olive (subdued),

all form perfectly harmonious combinations, because they each contain the three primaries in one form or another. For the same reason, a combination of the above nine colours would be equally harmonious.

Except in small patterns, the first two combinations given above are unsuitable for the best class of decorative prints. To most people their effect is crude and hard; their brilliancy dazzles rather than satisfies the eye, and they soon become wearisome. Conversely, the combination of brown, grey, and olive, while certainly restful to the eye, is somewhat lacking in character (unless one at least of its elements approaches to the brightness of a secondary colour), and usually requires to be relieved by the addition of a brighter colour. After all, however, the choice of a "colouring" is to a great extent a matter of taste, and is governed largely by the purpose it is intended to serve: if its surroundings are too bright and lively in colour, a calico print will be none the worse for being subdued, whereas in dingy localities a brightly tinted cretonne pattern supplies a real want, and satisfies a feeling for colour, which, if not always understood, is generally experienced.

But while the harmonious arrangement of colours in a design is a branch of calico printing, the importance of which can scarcely be overestimated, it is a branch quite apart from the actual compounding of printing colours, and one which to discuss with any profit would require a separate volume. It belongs essentially to the artistic side of the industry; and as it is concerned with the *appearance* of colours irrespective of their *composition*, its treatment here would be out of place, even if it were possible. In fact, the sole object of the foregoing brief review of some of the more important optical properties of colour and of colouring matters has been to show (*a*) why red, yellow, and blue are still regarded, in the arts, as primary colours; and (*b*) why the "undulatory theory" of light is of little help to the textile colourist. The results obtained by the mixing of *immaterial coloured lights* afford absolutely no indication as to what to expect from a mixture of similarly *coloured material bodies* —pigments, etc. Taken altogether, it is questionable whether any relation at all exists between the production of white light and the production of colour harmony; and it is certain that the establishment of the true theory of light and colour has not conduced to any improvement on the superb colour effects of either the old Venetian artists or the Oriental craftsmen in carpets and pottery.

Application of the foregoing Principles.

The accumulated experience, derived from centuries of practice in the mixing of all descriptions of colouring matters, has demonstrated beyond question that the colour of any material object can be imitated, more or less perfectly, by *suitable* shades of red, yellow, and blue, or mixtures of these. Practically speaking, this means that all colours consist of one or more of

the three colour elements, red, yellow, and blue; and therefore, starting out with these three, to which must be added the two extremes of non-colour—black and white—it ought to be possible to prepare an exact replica of any known shade. Further, every single shade of the infinite variety of colours met with in nature corresponds in qualitative chromatic composition with one of the following nine types:—Red, Yellow, Orange, Blue, Green, Purple, Brown, Grey, and Broken Green (Citrine or Olive); that is, all colours are either primaries, secondaries, or tertiaries.

The close relationship existing between the primary colours and their derivates, the secondaries and tertiaries, is clearly shown below. Thus—

THE PRIMARIES:—	Red, Yellow, Blue.				
THE SECONDARIES:—	Orange	=	Red	+	Yellow.
	Green	=	Yellow	+	Blue.
	Purple	=	Blue	+	Red.
THE TERTIARIES:—	Brown	=	Orange	+	Purple.
	Grey	=	Green	+	Purple.
	Olive	=	Green	+	Orange.

Brown is frequently called russet; and olive is also known as citrine and broken green.

Both the primaries and the secondaries occur in their purest form in the spectrum, and can be obtained by mixing suitable coloured lights, as well as from pigments and dyestuffs. On the contrary, the tertiaries can only exist in the presence of matter, and their formation depends entirely on the absorption of a considerable quantity of light. It is quite impossible to produce a tertiary colour by any mixture of lights. The addition of light to light only results in an increase of light, until finally pure white light is obtained; but the addition of the three primary colours to each other, in the form of pigments or dyestuffs, results in the destruction or absorption of light, and the consequent production of olive, brown, grey, or black, according to the strength and proportions of the colours used.

An analysis of the three typical tertiaries will show that they each contain red, yellow, and blue, and that they owe their difference in colour to the presence of an excess of one of these primary elements. Thus—

$$\text{BROWN} = \left\{\begin{array}{l}\text{Orange} = \left\{\begin{array}{l}\text{Yellow.}\\ \text{Red.}\end{array}\right.\\ \text{Purple} = \left\{\begin{array}{l}\text{Red.}\\ \text{Blue.}\end{array}\right.\end{array}\right.$$

$$\text{GREY} = \left\{\begin{array}{l}\text{Green} = \left\{\begin{array}{l}\text{Yellow.}\\ \text{Blue.}\end{array}\right.\\ \text{Purple} = \left\{\begin{array}{l}\text{Blue.}\\ \text{Red.}\end{array}\right.\end{array}\right.$$

$$\text{OLIVE} = \left\{\begin{array}{l}\text{Green} = \left\{\begin{array}{l}\text{Blue.}\\ \text{Yellow.}\end{array}\right.\\ \text{Orange} = \left\{\begin{array}{l}\text{Yellow.}\\ \text{Red.}\end{array}\right.\end{array}\right.$$

Red predominates in Brown.
Blue ,, ,, Grey.
Yellow ,, ,, Olive.

By varying the proportions of the primaries or secondaries, the above brown, grey, and olive may be made to approach as nearly as required to any of

their constituent colours; so that sometimes a brown may be almost indistinguishable from an orange or a purple; an olive may appear almost pure green, yellow, or orange; and a grey may assume the appearance of any colour, since it is easily affected by any variation of its constituents. Further, by mixing the primaries in certain proportions, it is possible to obtain a dense black which, when reduced in strength, yields a useful series of neutral greys. These greys or black are always formed, to a greater or less extent, in any combination of the three primaries, and it is to their presence that the dulness of the resulting tertiary colours is due. Hence tertiary colours of any desired shade can be obtained either by directly mixing the three primaries, or by simply adding the required quantity of previously prepared grey or black to the primary or secondary colours that are to be modified.

So long as a compound colour is composed of only *two* primaries it is a secondary colour, whatever its shade may be, or however much one of its components may be in excess of the other. A purple may be any shade between red and blue; but if it consist of these two colours only without the admixture of any yellow, it is a secondary colour whether it approximate to red on the one side or to blue on the other. Add the slightest trace of yellow, however, and it at once becomes a tertiary colour. The addition may be so small as not to produce any perceptible difference in shade, but, all the same, it results in the formation of a minute quantity of black, which absorbs a corresponding amount of light, and so reduces the luminosity of the mixture.

The dulling of a *secondary* colour by the addition of a minute quantity of its complementary *primary* is called technically "toning," and the modification of its shade by increasing one or other of its two component primaries is known generally as "shading." The combined toning and shading of one or other of the primaries, *or their typical compounds*, constitutes the whole art of colour mixing.

From the foregoing it might be supposed, and not unreasonably, that, given pure primary red, blue, and yellow colouring matters, it would be possible to reproduce exactly every conceivable shade of colour that is to be found in nature and the arts. But neither practical nor theoretical considerations afford the slightest support to any such supposition; for, in the first place, perfectly pure primary colours do not exist except in the spectrum; and secondly, if they did, they would, on theoretical grounds, be totally unsuited for use in mixtures.

Impure primary colours, therefore, possess the qualities of their defects: their employment is not only demanded by theory, but is absolutely unavoidable in practice, because no others are available. But, for a given purpose, their impurity must be of a certain kind, otherwise they yield unsatisfactory results. Hence, in practice, the shades of the red, blue, and yellow elements used in the making of compound colours vary according to the class of colour required. Thus a red inclining to orange and a blue inclining to green would, when mixed together, produce a very dirty shade of purple (if not a brown), whereas if a bluish-red and reddish-blue were employed the resulting purple would be bright and pure. So also scarlet and a warm yellow give the brightest oranges, and greenish-yellow and greenish-blue the purest and most brilliant greens.

In a less degree, the same thing applies to tertiary shades, although in these it is easily possible to adjust the balance of the primaries. Still, in some cases it is difficult to match even a tertiary colour if its elements all possess the same kind of impurity. For instance, take the case of a warm orangy-brown: if its components consist of a crimson, a lemon-yellow (greenish-yellow), and reddish-blue, it is out of the question to expect anything approaching to the

shade required; but if the crimson and lemon-yellow be replaced by scarlet and maize-yellow, the desired effect is obtained at once, because the excess of blue is eliminated.

Similarly, in olives excess of blue and red must be avoided; and in greys the blue element must always predominate, unless, of course, the grey is intended to be quite neutral.

Any group of colours employed in the making of an extensive range of compound colours may be most conveniently called a "series," and for the sake of distinguishing it from all other series it might be lettered thus, "Series A," etc. In a series of the three primary colours the red ought to be first, the yellow second, and the blue third; and this order ought to be preserved for every other series, whether its members be pure primaries or compound shades. If a fourth member is introduced, it ought to occupy a position between the two colours it most resembles. Thus—

A three-member Series.	*A four-member Series.*
1. Red element.	1. Red element.
2. Yellow element.	2. Yellow element.
3. Blue element.	3. Green element.
	4. Blue element.

The first number denotes the Red element. " second " " " Yellow element. " third " " " Blue element.	In the first series (three-member).

Thus, calling the first series A, an olive written in the following manner—Olive 1.6.2 A—would imply that it was composed of 1 part of red, 6 parts of yellow, and 2 parts of blue. Any number written after the letter A would denote the extent to which it was diluted by the addition of thickening.

OLIVE 1.6.2 A 4.=	1 part	Red.
	6 parts	Yellow.
	2 "	Blue.
	36 "	thickening or reduction.

Here the full-strength olive consists of 9 parts by weight or volume; and as the final number (4) after the A indicates that 1 part must be diluted or "reduced" by 4 parts of thickening, the total amount of this latter is therefore 4×9, or 36 parts. It may be 36 gallons, quarts, pounds, or kilogrammes, according to the standard in use.

By far the greater number of compound colours in general use are quiet tertiary shades; and as these can be mixed as well from secondaries, or even from other and comparatively bright tertiaries, as from primaries, it is by no means essential that the members of every series should consist of primary colours, or of colours approximating to primaries. Indeed, with the exception of bright oranges, purples, and yellowish-greens, very few compound colours call for the use of primary colours at all. Hence in practice the red element varies between orange and reddish-purple, the blue element between green and yellow, and the yellow element between yellowish-orange and lemon-yellow. Within these limits all shades of colour may be used in different series intended for the production of browns, olives, greys, drabs, fawns, terracottas, buffs, and mode shades of every description.

In making use of abstract colours to illustrate the foregoing system of colour mixing, it has been impossible to give more than a rough indication of the composition of the several representative types of compound colours. The following concrete examples will supply this deficiency, the percentage of each

dyestuff contained by the separate elements of each series of colours being given, together with the mordant used. The amount of mordant and the kind of thickening used must be determined by the properties of the dyestuff and the style of work in hand. When alterations in thickening are desired it is usual to indicate these by adding additional letters to the colour after the reduction number; thus Olive 1.8.2 A 4 G.T. means that the whole colour is thickened with gum tragacanth—the abbreviation G.T. being the initials of the thickening agent. Similarly, G.S. and G.A. represent gum Senegal and gum Arabic respectively; and so on for any other special thickening. The absence of any letters after the reduction number is usually taken to mean that the colour is made up with starch paste.

Series of Colours for Compound Shades.

General Rules of the Series.—In series of three members the colours are always arranged as nearly as possible in the order in which their types occur in the spectrum. This is a matter of convenience only, and may be modified at will; but it enables the composition of a shade to be recognised more readily if every colour is worked on the same general principle. In four-member series the same rule is observed, the only difference being in the manner of writing the colours on the printer's work sheet. Each series is given a distinctive letter or letters; the composition of the colours made from it is denoted by figures following the name of the colour; the order in which these figures occur corresponds to the order of the members in the series, and their value represents the relative proportions of the constituents of the compound colour they yield. The reduction of the strength of a colour is indicated by the final number after the distinctive series letter. Thus a series containing Orange, Yellow, Green, and Blue may bear the distinctive mark of X, and a brown written as Brown 4.2.0.1 X. 20 would consist of—

$$\left.\begin{array}{l}4 \text{ parts Orange X} \\ 2 \;\;,, \;\;\text{Yellow X} \\ \;\;\text{No Green and} \\ 1 \text{ part Blue X}\end{array}\right\} = 7 \text{ parts.}$$

140 parts starch paste = (7 × 20).

Or put it this way:

Name of Colour.		Constituents. Orange.	Yellow.	Green.	Blue.	Series.	Reduction.
Brown	=	4	2	0	1	X	20
Olive	=	1	6	6	1	X	..
Gold	=	1	8	0	0	X	10

In this manner, once the constitution of a series is known, it is possible to ascertain at a glance the composition of any colour derived from it; and thus the work of the colour mixer is both simplified and expedited, since it is much easier to remember a few series of colours than hundreds of disconnected and unsystematic recipes.

With from twenty to thirty well-selected series it is possible to match practically any compound shade that is ever likely to be required in ordinary steam styles.

The series given below will serve as examples of the methods adopted on a works scale. They are in actual use, and have yielded consistently good results in practice.

SERIES A.L. (Steam mordant colours).

1st. Red A.L. [10 per cent. Alizarin (blue shade, 20 per cent. paste), alumina mordant].
2nd. Yellow A.L. (30 per cent. Persian berry ext. 48° Tw., chrome mordant).
3rd. Green A.L. (15 per cent. Alizarin green, chrome mordant).
4th. Blue A.L. (6 per cent. Alizarin blue S., „ „).

Examples :—

Olive 1.6.6.1 A.L.
Brown 6.4.1.1 A.L.
Grey 1.2.1.8 A.L.
Salmon 10.2.0.0 A.L. 5.
Buff 3.10.0.1 A.L. 12.
Chocolate 8.1.2.1 A.L.
Fawn 5.6.1.0 A.L. 5.
Old Rose 11.0.0.1 A.L.
Claret 11.0.1.0 A.L.
Old Gold 1.10.0.1 A.L. 5.
Drab 3.6.0.3 A.L. 5.
Gobelin Blue 0.0.10.2 A.L. 2.

Etc., etc.

SERIES B.

1st. Orange B. [15 per cent. Alizarin orange (20 per cent.) with chrome].
2nd. Yellow B. (10 per cent. Chromocitronine R., chrome mordant).
3rd. Green B. (4 per cent. Alizarin viridine (powder) chrome mordant).
4th. Blue A.L. (see above).

Examples :—

Apple Green 0.2.1.0 B. 10.
Fawn 2.1.1.0 B. 6.
Brown 4.2.0.1 B.
„ 4.6.0.1 B.
Mode 1.2.0.1 B. 10.
„ 3.3.0.2 B. 10.
Olive 1.3.6.1 B.
Reseda 1.0.4.0 B. 8, etc.

SERIES C.

1st. Purple C. (4 per cent. Chrome violet with chrome mordant).
2nd. Yellow C. {7½ per cent. Bark extract / 7½ per cent. Persian berry extract} with chrome mordant.
3rd. Blue A.L. (see above).

Examples :—

Grey 1.1.6 C. 10.
Violet 6.0.1 C. 10.

SERIES P.B. (for pigment blotches).

1st. Red P.B. (10 per cent. Vermilion with albumen and tragacanth).
2nd. Buff P.B. (10 per cent. Yellow ochre with „ „ „).
3rd. Blue P.B. (5 per cent. Ultramarine „ „ „ „).
4th. Black P.B. (10 per cent. Lampblack „ „ „ „).

Examples :—

Salmon 6.1.0.0 P.B. 6.
„ 9.1.0.0 P.B. 6.
Drab 3.8.0.1 P.B. 6.
Silver grey 6.0.6.5 P.B. 6.
Fawn 5.8.1.1 P.B. 6.
Lavender 6.0.6.0 P.B. 6.
Slate 1.0.3.0 P.B. 6.
Electric blue 1.0.9.0 P.B. 6.
Linen 1.8.1.0 P.B. 6.
Stone 0.3.0.1 P.B. 6.

SERIES B.C. (Basic Colours).

1st. Pink B.C. (2 per cent. Rhodamine 6 G. with tannic acid).
2nd. Yellow B.C. (2 per cent. Auramine O. conc. „ „).
3rd. Blue B.C. (2 per cent. Methylene blue N. „ „ „).

Examples :—

Orange 1.4.0 B.C.
Green 0.6.1 B.C.
Violet 1.0.1 B.C.
Olive 1.12.2 B.C.

SERIES D.

1st. Claret D. [15 per cent. Alizarin, yellow shade (20 per cent.), with chrome mordant].
2nd. Yellow C. (see series C).
3rd. Blue A.L. (see series A.L.).

Examples :—

Terra-cotta 1.2.0 D.	Drab 1.3.1 D. 10.
Old Gold 0.24.1 D. 8.	Fawn 1.6.1 D. 10.
Claret 1.0.0 D.	Brown 2.4.1 D.
Plum 4.0.1 D.	Grey 1.4.8 D. 10.
Lilac 1.0.4 D. 10.	Olive 0.4.1 D. 1 etc.

In a similar manner series can be made from any class of colouring matter that is capable of being applied by printing. For this purpose, therefore, the Direct colours, the Sulphur colours, and the various Vat colours are all suitable. A useful series of the last group is as follows :—

SERIES I.

1st. Durindone red B.S. (20 per cent. with potassium carbonate and Rongalite).
2nd. Caledon yellow G. (15 per cent. with potassium carbonate and Rongalite).
3rd. Caledon blue R.S. (15 per cent. with potassium carbonate and Rongalite).

Examples :—

Green 0.1.2 I.	(Light) Green 0.1.2 I. 3.
Red 1.0.0 I.	
Purple 2.0.1 I.	
Brown 4.2.1 I., etc.	

The above half-dozen or so series will be sufficient to show with what facility it is possible to obtain a vast variety of shades by simply altering the proportions of the few constituent colours. Examples could be multiplied, but the above will serve to illustrate the principles of the method—a method which, with such modifications and amplifications as the common sense of the colourist will suggest, may be applied to any and every style of work in which compound colours play an important part.

While a series consisting of three members—red, yellow, and blue—contains all the elements essential to the production of shades belonging to every known class of colour, it is found in practice that four-member series are more generally useful, because more variety can be got out of them. The addition of a fairly bright green, such as Alizarin viridine, for instance, considerably increases the scope of a series, and enables very pure shades of quiet Gobelin blues and greens to be produced free from flatness.

In the mixing of tertiary shades of any description it is advisable, on practical grounds, to avoid, as far as possible, the use of unnecessarily bright colours. If such brilliant colours as Rhodamine, Auramine, Malachite green, and Methylene blue have been mixed together to give a complex mode shade (olive, fawn, drab, grey, etc.), it will be found, on making a second batch, that the slightest excess of any one of them over the amount previously employed will make a tremendous difference in the resulting shade of colour; and that, as a rule, it is extremely difficult to get the same shade twice alike, more especially if it be light and of a delicate tone. Colours that are composed of three or

more bright luminous colours are always very difficult to match accurately, and accordingly they ought never to be made, except for special styles in which only one class of dyestuff is available—*e.g.* the tannin discharge style, for which only basic colours can be used. Even then, if quiet mode shades are required, it is better, if possible, to execute the work by some other process—say the chlorate discharge on slop-padded mordant colours, or by dyeing Alizarin colours on discharged chrome mordanted cloth—which will allow of the same effect being produced by more reliable means.

On the other hand, if the bright, pure, luminous colours are replaced by more subdued colours, such as Alizarin, Alizarin orange, Persian berries, Quercitron bark, Alizarin yellows, Alizarin viridine, Alizarin blue, etc., in combination with chromium mordants, the shades produced by their combinations are much easier to match and to bring up to standard, because a slight excess of any one of them does not produce anything like so decided an effect as when the brighter dyestuffs are used.

Further, in order to prevent undue loss of harmony in the colour scheme of a multicolour pattern when seen under gaslight, etc., all the compound shades in the pattern ought to be made, as far as possible, from the same constituents, *i.e.* the same series of colours. By this means the absorption spectra of the olives, browns, golds, drabs, or greys used in the colouring will be more or less similar to each other (though the composition of the colours differs, of course; yellow predominating in the golds, blue in the greys, red and yellow in the browns, and blue and yellow in the olives); that is to say, rather, that they will bear the same approximate relation to each other in gaslight as they do in daylight; and therefore, although the colouring may differ considerably from the daylight effect, it will at least not lose a great deal in balance or harmony. But if widely *different* constituents are used for the *various* compound shades, it is more than likely that what appears perfectly harmonious in daylight will in gaslight become a mere botch of badly-balanced and inharmonious colours.

The same chaotic effect is produced, under any conditions, in course of time, if the component parts of the several compound shades do not possess about equal powers of resistance to the action of light, soap, and other agencies. Many beautiful colours fade to quite horrible shades; others wash out almost immediately; and others, again, lose their purity and freshness when diluted or reduced. When such colours are mixed with others which are much faster, to make compound shades, these latter rapidly alter when exposed to light, or they may be changed completely by the first washing, the result in either case being that the whole balance of the colour combination in the pattern is upset and its effect completely spoiled. Too much attention, therefore, cannot be paid to the selection of the members of a series if the best and most durable results are to be obtained.

In testing a group of colours for mixing properties, their fastness to light, soap, chlorine, and perspiration (acetic acid) ought to be compared, their suitability for working with a common thickening ascertained, and a range of gradated tints of each colour prepared, so as to make sure that no colour is employed which alters in tone on reduction.

The advantages of working according to some such system as that outlined in the preceding pages are that (1) fewer standard colours are required; (2) the composition of any compound shade can be seen at a glance; (3) the nomenclature of colour mixing is simplified, and at the same time made more graphic; (4) the particulars of the whole of the colours used in a works can be entered up in a comparatively small book, thus doing away with the folios that accumulate so rapidly in colour shops, where every little mixture is given a special name which affords no clue to its composition; (5) the saving of time, arising

out of the fact that thousands of shades can be made without necessitating a single reference to a notebook; (6) the disorganisation of work, which frequently happens when a change is made in the *personnel* of a colour shop, is reduced to a minimum; and (7) that with a few well-selected series of colours it is possible to obtain an infinite variety of shades, each one of which possesses properties more or less identical with those of all other shades mixed from the same elements. If these elements have been chosen with care every colour made from them—olives, browns, greys, fawns, drabs, salmons, etc.—will be equally fast, so that an elaborate colour scheme can be built up entirely from three or four simple colours, without any fear of one colour fading or washing-out more than another. Of course, light colours are always apt to fade more rapidly than dark ones of the same composition, but, apart from this common defect, colours of the same series behave in the same way; and if care has been taken in the first instance to select the *fastest* colours available for a given class of work, it is possible to obtain a range of pale shades that compare favourably in fastness to light with the standard colours from which they are mixed. Altogether, the unequal fading of a combination of colours of similar composition is not so pronounced as to detract from the system of colour mixing just described; in fact, experience has demonstrated that multi-coloured prints worked on the above methodical lines preserve their balance in a remarkable degree.

Many exceedingly valuable colouring matters cannot be worked in series; but these are, for the most part, used for special purposes; and as they are unsuitable for the preparation of compound shades, they call for no mention here.

The few examples of series already given are only suitable for steam work, but the same principle can be applied to any other class of work, and in the following pages other illustrations of its varied usefulness will be found in the descriptions of the discharge styles, etc.

Useful series can be made from all classes of dyestuffs, and for any style of printing in which compound shades are used. Once the simplicity, convenience, reliability, and scope of the systematic method of colour mixing outlined above are recognised, its advantages over the haphazard methods still in use in many printworks will be obvious.

It must be understood, however, that a mixture of colours is never employed if the desired result can be obtained by using a single colouring matter; for all mixtures are liable to irregularity.

The introduction of the coal-tar colours not only revolutionised textile colouring in general, but in particular resulted in raising the Direct Printed or Steam Style from a position of insignificance to one of paramount importance. Almost every addition to the now enormously long list of coal-tar colouring matters increased the range of effects producible by means of direct printing; and at the present time it is scarcely too much to say that work executed by this method forms by far the greater proportion of the total sum of calico and other textile fabrics printed on the large scale.

(2) THE DYED STYLE.

The "dyed style" is the oldest, and is still one of the most important, of all the numerous styles of printing in use at the present time. In a simple and primitive form it was largely practised by the ancient Hindoos, Chinese, and Egyptians, many of whose methods are still in use in the East Indies; similar methods are also employed by the natives of the West Coast and in

the interior of Africa. In Europe and America, however, the dyed style has been brought to a high pitch of perfection, and, in common with other branches of calico printing, its development has proceeded on scientific lines.

Chemical research has not merely disclosed, but has improved upon the most cherished secrets of the old-time dyer; so that nowadays anything of value that he knew is to be found in almost any good textbook, and many of the things that he practised have been discarded as utterly worthless. At the same time good *practical* dyers are just as necessary as ever they were; for, although the art of dyeing has been shorn of the mysterious, it is by no means a craft that can be taken up by a chemist fresh from the university. It requires a good deal of experience to dye even a regular plain shade in large quantities; and when the process is complicated by the presence of different strengths of mordants, the necessity for keeping the white parts of printed goods clean, and the matching of shades on different qualities of cloth, it requires a good deal more than laboratory practice to produce successful results.

The dyed style differs from the direct printed or steam style in the manner of applying the colours to, and fixing them upon, the cloth. Instead of the colours and their mordants being mixed together in a thickened paste, printed simultaneously on the cloth and fixed at the same time by a process of steaming, they are applied separately and in two quite distinct stages, each of which comprises a series of operations peculiar to itself. These stages are known respectively as Mordanting and Dyeing. The former may be effected either by printing a thickened mordant in the desired pattern on the cloth, or by slop-padding the cloth in a solution of the mordant, and afterwards discharging it with an "acid" in the required pattern. In both cases the object is the same, viz. to fix a mordant on the cloth *locally*, so that when it is afterwards treated in dye liquor the dyestuff will only attach itself permanently to those parts of the cloth to which the mordant has been applied. The *dyeing operation* may be performed in any convenient form of apparatus. That usually preferred for the general work of calico printing is the spiral dye beck already described; but for certain styles the jigger may also be used with advantage; and for very heavy goods, like molletons, corduroys, and velveteens, the old-fashioned wince dye beck cannot be improved upon when large quantities are dyed at a time.

The dyed style may be produced in different ways according to circumstances, but the following will afford the simplest illustration of the practical application of the principles involved. The cloth is first printed, either by block or roller, with one or more thickened mordants. The composition of the mordants will vary with the colour to be dyed. After drying, the mordants are fixed in a suitable manner; the cloth is then well washed, and finally dyed by being passed into a hot solution of dyestuff, through which it is made to circulate continuously until the required depth of shade is attained. During this operation the dyestuff combines with the mordant or mordants to form an insoluble colour lake or lakes analogous to those obtained by the very different method of steaming. On leaving the dye bath the whole surface of the cloth is more or less stained with colour; but that on the unprinted (*i.e.* unmordanted) portions only adheres mechanically, and can be entirely removed by washing and soaping the goods, thus leaving a coloured design on a white ground.

From the foregoing it will be seen that the essential operations in the dyed style are: (1) the printing-on of the mordant, or its application in some other way; (2) the fixing of the mordant; (3) washing out the excess of the fixing agent; (4) dyeing; and (5) washing and soaping the dyed cloth to

remove all loosely adhering colour, and to clear the white parts of the pattern. These five operations, with such modifications and additions as are demanded by circumstances, are common to all the numerous phases of the dyed style.

The terms *dyed style*, *dyed work*, and *dyed way* were formerly applied exclusively to goods mordanted with iron and aluminium salts, and dyed up afterwards in Madder, Logwood, Quercitron bark, and other vegetable dyestuffs. At the present time no such distinction exists; and the dyed style now comprises all classes of work in which any mordant whatsoever is first applied to the cloth, and subsequently combined in the dye bath with a colouring matter capable of forming an insoluble coloured compound with it.

Most of the colours used in dyeing can also be (and are) applied by direct printing. Hence the dyed style is not so much characterised by the use of special colours and mordants as by the methods employed in their application to, and fixation upon, the cloth. Nevertheless the kind of colour employed influences the *modus operandi* of dyeing to a considerable extent. Different classes of colouring matters and mordants demand different treatments; and as these treatments point to so many variations of process, the dyed style does not consist of an unalterable sequence of operations, but of several quite distinct processes. Of these the most important are the following:—

(*a*) The Madder style and its modifications.
(*b*) The Basic style.
(*c*) The Chrome Mordant style.

A slight modification of the Madder style allows of any basic aniline colour being dyed on cloth mordanted for Alizarin colours—a facility permitting of cloth printed in a single mordant being dyed up in an immense variety of shades, including those obtained from Alizarin, basic colours, and most of the vegetable dyestuffs still in use.

(*a*) **The Madder Style.**—This style owes its name to the fact that formerly Madder was the chief dyestuff used in its production. It still retains its old name, although Madder has been superseded entirely by its artificial competitor, Alizarin, which, chemically, is identical with the essential red colouring principle of the madder root.

The Madder style is the oldest, the most important, and the most largely practised of the dyed styles at present in vogue. It yields an extensive range of exceedingly fine colours, fast both to light and soap; and it possesses an advantage over all other printed and dyed styles in that various shades of red, pink, maroon, chocolate, and purple, together with black, can all be associated in a multicolour pattern, and dyed simultaneously by *one operation* and with the *single dyestuff, Alizarin.*

In these multicolour effects, advantage is taken of the property possessed by Alizarin of forming differently coloured lakes with different mordants. Thus the colour of the lake produced with aluminium salts is red; with iron salts, black or purple, according to the strength of the mordant; and with mixtures of iron and aluminium mordants, various shades of maroon, which become chocolates as the proportion of iron increases. Other colours, such as Chrome yellow, Catechu brown, Alizarin blue, and Indigo may also be introduced into multicolour prints, but they require special treatment, and the blues especially require careful handling when used in combination with Chrome yellow, although formerly Indigo was largely used in this connection.

The only mordants used on the large scale in the madder style are the *crude* acetates of iron and aluminium—the black liquors and red liquors of commerce. The properties and composition of these mordants have already been discussed, but it may not be out of place here to recapitulate the practical

reasons for preferring the crude impure salts to the pure normal acetates. In the case of iron, the pure salt not only oxidises very rapidly in solution, but when printed it oxidises both irregularly and to a point beyond that at which good results are obtainable. As previously noted, the best colours can only be dyed on an iron mordant when it exists on the cloth in a condition intermediate between the ferrous and ferric states. When pure ferrous acetate is employed, its conversion into the highest state of oxidation takes place so rapidly that, in practice, it is found impossible to control it sufficiently well to enable it to be used with any degree of certainty. On the other hand, the crude pyrolignite of iron or "black liquor" contains organic impurities which, while not detracting from the beauty of the final shade, retard the rate of its oxidation to such an extent that under proper conditions it is possible to arrest it at exactly the point required to secure the best effect. Aluminium only forms one oxide (Al_2O_3), and so cannot be over-oxidised; but it also forms various basic salts, each of which possesses a different affinity for Alizarin. If, therefore, the mordant used for printing decomposes very readily, it is apt to produce salts of varying basicity on the cloth, and hence to yield irregular shades on dyeing. Experience has proved that pure aluminium acetate yields neither such regular results nor such full rich colours as an acetate in which a portion of the acetic acid is replaced by sulphuric acid, *i.e.* a sulphate-acetate. Moreover, pure acetate of alumina decomposes on standing, and loses strength by depositing alumina or an insoluble and very basic acetate; access of light accelerates the rate of this spontaneous decomposition. Again, when thickened and printed, the pure acetate is very susceptible to the action of dry heat, and is easily dehydrated by too great a temperature in drying after printing; it also possesses the property, when dried on the cloth, of repelling water, so that in dunging it prevents the fixing liquors from penetrating into the body of the material, and thus gives rise to another cause of irregular work. These defects can be overcome by the addition of acetic acid to the normal acetate; but care must be taken to avoid making it too acid, as otherwise it does not thicken well, and works badly owing to its solvent action on the edge of the steel doctors. On the whole, therefore, a crude acetate or "red liquor," made from sulphate of alumina and calcium acetate, and corresponding approximately to the formula $Al_2(SO_4)(C_2H_3O_2)_3(OH)$, is preferred to the normal salt, since any precipitate it may deposit on boiling with the thickening re-dissolves on cooling, and in printing, drying, ageing, and dunging it behaves, as shown by experience, in a satisfactory manner.

In any case, excessive heat in drying must be avoided, otherwise all iron and aluminium mordants are liable to be dehydrated (tech.: *burned*), in which state their affinity for colouring matters is reduced considerably, and they yield poor, thin shades in the dye bath.

After printing and drying, the next stage in the production of Madder work is the fixation of the mordants on the cloth. For this purpose the printed goods are first aged and then dunged. During the ageing the thickening materials are softened, allowing the mordant to penetrate thoroughly into the fibres of the cloth; large quantities of acetic acid are evolved, and the mordant is converted into a more or less insoluble basic salt which adheres or is fixed firmly to the cloth. The dunging process completes the fixation of the mordant by precipitating those portions of it which have been unacted upon in ageing; it also prevents the unprinted parts of the cloth from becoming mordanted by any soluble mordant running into them from the printed parts during the subsequent operation of dyeing; and finally, it removes all the thickening used in printing, thus leaving the cloth perfectly free to the action of the dyestuff. If any thickening were allowed to remain it would act as a

mechanical resist, by interposing an obstruction between the mordant and the dyestuff.

As previously stated, the process of ageing consists in exposing the printed goods to the action of warm moist air for varying periods, the duration of which depends on the work in hand. The process, and the precautions to be observed, have been discussed at length in another part of the present volume, under the heading of "The Treatment of Goods after Printing," and little more remains to be said on the subject. Any of the methods there described may be adopted, but for general work Crum's Ageing Machine is the most convenient; its action is intermediate between that of the hanging room and the Mather & Platt Rapid Steamer or Steam Ager; it is quicker than the one, and more reliable, on the whole, than the other, especially for iron mordants, which require very gentle oxidation if the best results are to be secured. The time required to pass through Crum's continuous ageing chamber is twenty minutes, and the state of the atmosphere ought to correspond with about 36° C. dry-bulb and 33° C. wet-bulb thermometers. On leaving the ageing chamber, the goods are loosely bundled in 2–4 piece lots and allowed to lie for several days in the room surrounding the chamber. The temperature of this outer room is usually maintained at 33° C. dry- and 29° C. wet-bulb thermometers, or as close as possible to these points. In this way the ageing process is completed with the least possible trouble, and without taking up anything like the immense amount of space occupied by the old-fashioned hanging rooms. For aluminium mordants, either alone or in combination with Aniline black, the rapid ager may be used if desired. The time required in passing through the chamber is from two to four minutes, through an atmosphere of low-pressure steam at a temperature of 75° C. to 90° C. In other respects the process is identical with the preceding.

Dunging has likewise been described in detail in the earlier pages of this work, and nothing more need be said about it beyond giving a few particulars of the composition and working of the dunging liquors used in illustrating the practical examples of the Madder styles, which are to follow later.

After ageing and dunging, the goods are dyed in any convenient manner and with any suitable dyestuff.

Washing, soaping, and clearing follow the dyeing operation; and as these processes vary with different classes of work, their description will be given along with that of the practical methods.

By far the greater proportion of dyed work produced at the present time consists of single-colour patterns in red, chocolate, and purple. Black and white styles were also produced in large quantities at one time by dyeing Logwood on a strong iron mordant, but steam Aniline black has now displaced Logwood almost entirely for this purpose, and also for most Madder styles in which black occurs in combination with red, pink, chocolate, and purple. With very few exceptions, all multicolour patterns, containing more than two or three shades of a colour or colours, are nowadays executed by the steam style. Occasionally a combination of red, pink, chocolate, purple, and black is produced in the dye beck, but the style is practically obsolete, although it yields exceedingly fast and very pleasing effects.

The thickened mordants used in the Madder style are called *colours* not because they contain any colouring matter, but because they give definite shades when dyed up in Alizarin. Thickened red liquor is always known as "red" in the colour shop, although it gives different colours with different dyestuffs—*e.g.* yellow with Bark extract and Persian berries; blue with Alizarin blue; purple with Gallo-purple or Gallo-cyanine; and brown with Anthracene-brown. Similarly, thickened iron mordants are known as blacks or purples

according to their strength; and mixtures of iron and aluminium mordants generally go under the name of chocolates. This is simply because their chief use is for the production of these colours with Alizarin.

Madder Red.—Print on white unprepared cloth the following red:—

6 T. RED.[1]

100	grms.	wheat starch.
50	„	flour.
900	„	red liquor 6° Tw.
20	„	olive oil.
·5	„	Magenta.

Boil, cool, and add—

12·5 grms. tin crystals.

1000 after cooling.

The stannous chloride (tin crystals) is added to prevent the fixation of any iron, which would, of course, dull the shade of the red by forming a small quantity of purple in the dye bath; and the Magenta is merely added for "sightening"; that is, to give a decided colour to the paste, so that the printer can see what he is doing. The sightening all washes out in dunging.

After carefully drying, the goods are aged and then dunged as under:—

FIRST DUNGING.

The goods are passed at *full width* through the fly dunging machine (see page 174), the first three compartments of which are filled with the following liquor:—

2000	litres	water,
15	kilos.	chalk,
2½	„	phosphate of soda,
70–85	„	cow-dung,

and the last with water alone.

The treatment occupies 2–5 minutes and is conducted at a temperature of 60° C. After washing, the goods are dunged a second time, in the rope form, in the following:—

SECOND DUNGING.

500	litres	water.
1½	kilo.	chalk.
¼	kilo.	phosphate of soda.
8–12	kilos.	cow-dung.

This liquor is contained in a spiral dunging beck, similar to a dye beck; and the goods are worked in it for 20–30 or more minutes at a temperature of 50°–60° C. After a thorough wash, to remove completely every trace of the dunging solution and the thickening materials, the goods are ready (without drying) for dyeing.

In works where large quantities of Madder-dyed goods are regularly produced, the second dunging is performed in a continuous manner. For this purpose three or more becks are arranged to work together, the cloth passing from the first into the second, from the second into the third, and so on through the whole range.

Cow-dung imparts a somewhat yellowish-green appearance to the mordanted parts of the cloth, especially if used in excess, but as a rule the tint is too slight to affect the shade of deep colours. It may be strong enough, however, to dull

[1] **6 T. Red denotes that the colour is made from red liquor at 6° Tw.**

the brightness of light reds and pinks; and where this is to be suspected from the general appearance of other goods, one of the many dung substitutes may be used with advantage.

Of these, the most commonly employed are phosphate of soda, binarsenate of soda, silicate of soda, and sometimes, though rarely, silicate of lime. Chalk is an ingredient common to nearly all dunging liquors, and occasionally, too, a small quantity of ammonia is added. The following solutions may be taken as typical of the composition of these dunging liquors:—

	I.	II.	III.	IV.	
Phosphate of soda .	1½–6	..	..	..	parts by weight.
Binarsenate of soda .	..	2·5	..	..	"
Silicate of soda 32° Tw. .	..	..	20	..	"
Silicate of lime . .	..	..	..	1000	(saturated solution).
Chalk	7½	7½	7½	7½	parts by weight.
Water . . .	1000	1000	1000	..	"

Silicate of soda is not generally employed as a dunging agent on account of its liability to contain an excess of alkali, either in the form of free caustic soda or carbonate of soda. Properly prepared, however, and free from this defect, it may be used with safety, even for weak aluminium mordants. Taken altogether it is, however, perhaps the least suitable fixing agent for aluminium mordants, since the resulting colours are neither so bright nor so full as when the other dung substitutes are employed.

Silicate of lime is an extremely insoluble salt, and to ensure an efficient dunging by its means the bath must always contain an excess in order to keep up its strength.

It frequently happens that the thickening materials of printing pastes are difficult to remove in dunging, especially if the cloth has been printed in a heavy pattern, in thick colour, and with newly engraved rollers. In such cases the most effectual method of removing the thickening is to add malt or bran to the dunging liquors, and to prolong the second dunging operation. Thus—

First Dunging.

60° C. { 2000 litres water.
35 kilos. good quality silicate of soda 32° Tw.
4 " phosphate of soda.
30 " malt or bran.

Second Dunging.

60° C. { 500 litres water.
2 kilos. chalk.
¼ kilo. phosphate of soda.
5 kilos. malt or bran.

If, after 45 minutes' treatment in the second dung liquor, some of the thickening still adheres to the goods, it can be finally removed by working them for 15 minutes in an infusion of malt or bran at a temperature of 50°–60° C. The diastase ferment of malt and bran acts on the starch, converting it into easily soluble sugars.

When cow-dung is used it is rarely necessary to add malt or bran to the dunging liquors, since, in addition to fixing the mordants, cow-dung also acts energetically on the thickening materials used in printing, and renders them

soluble in warm water. On the whole, cow-dung is the favourite fixing agent with practical dyers; and it must be admitted that, taking everything into consideration, it yields the best and most regular work. Experience proves that, other things being equal, cow-dung acts effectively, and imparts a softer feel to the cloth in less time than any other dunging agent yet discovered. Its only drawbacks are, that it is irregular in composition, that it sometimes stains the cloth, and that it requires changing more frequently than the soluble dung substitutes cited above. Properly handled, however, it gives excellent results, both as regards depth and quality of colour.

After a thorough wash in any type of spiral washing machine, the properly dunged goods are split up into conveniently sized lots and dyed in Alizarin together with certain additions, such as sumach, tannic acid, glue size, Turkey-red oil, and chalk—the latter being employed only if the water be deficient in lime, the presence of which is absolutely essential to the production of a bright red. The sumach or tannic acid tends to increase the fastness of the colour, and in conjunction with the glue size prevents the white parts of the pattern from becoming unduly stained; the Turkey-red oil, which should contain a fair quantity of free fatty acid, enhances the beauty of the shade, increases its depth, and promotes the penetration of the Alizarin into the body of the cloth.

The composition of the dye bath and the proportions of its constituents vary with the strength and quantity of the mordant printed on the cloth. A small-spot pattern requires a much weaker dye bath than a heavy stripe printed in the same colour, and the same pattern printed in two colours of different strengths requires the dye bath to be regulated accordingly. Thus 6 T. Red (Aluminium acetate 6° Tw.) requires really six times as much Alizarin as 1 T. Red which is six times weaker, and similarly for all other strengths of mordants. If an excess of dyestuff is employed, there is always a risk of the whites being badly stained. In order to avoid this as much as possible, the proportion of glue size is increased for patterns containing large masses of white, such, for instance, as widely-set spot patterns. On the other hand, when the entire surface of the cloth is printed, as in many furniture patterns, the use of glue may be dispensed with altogether.

For an average kind of pattern, covering about half the surface of the cloth, and printed in the 6 T. Red already given, the following dye bath will be about correct.

DYE BATH (for 100 kilos. of cloth).

5500 grms. Alizarin 20 per cent. paste.
$\left\{\begin{array}{l}\text{1000 ,, glue.}\\ \text{2000 ,, water.}\end{array}\right.$
2000 ,, Turkey-red oil (3 parts neutralised).[1]
750 ,, chalk.
550 ,, dried and powdered sumach.
2000 litres water.

The pieces, in the rope state, are run into a spiral dye beck containing the above ingredients. They are dyed in the cold for 15 minutes, then the temperature is gradually raised in 15 minutes to 40° C., and after another 20 minutes to 60° C., and finally, after dyeing at 60° C. for 20 minutes, to 75° C., at which temperature the goods are worked for 15–20 minutes. They are then taken out and well washed through a series of square beater machines (see p.

[1] The Turkey-red oil is not essential at this stage, and may be omitted if desired. Its inclusion in the dye bath has been characterised as irrational, but, as it gives excellent results in practice, this opinion may be disregarded.

188). If the whites are not satisfactory, the goods are then further treated in an infusion of bran (2 per cent.) for 15 minutes at 75°–90° C., and then thoroughly washed and hydro-extracted, or, if they cannot be dealt with at once, dried.

At this stage the colour of the dyed pieces is a dull brown red, totally unlike an Alizarin red. To convert this dull Alizarin alumina lake into a full rich and bright red, the goods are oiled, steamed, and finally well soaped until the whites are pure.

Any of the ordinary soluble oils of commerce may be used for brightening dyed reds, but a much better result is obtained by using one of the specially prepared oil mixtures containing tin and oxalic acid. Of these, the two given below have yielded excellent results on the large scale.

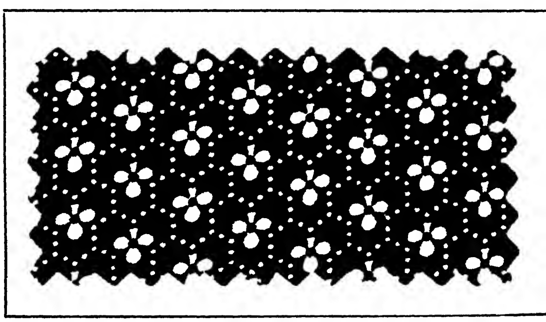
BRIGHTENING OIL I.

200	grms.	Turkey-red oil 25 per cent. (sodium sulphoricinoleate).
15	,,	stannous sulphoricinoleate (*q.v.*).
15	,,	ammonia.
125	,,	oxalate of ammonia 3° Tw.
645	,,	water.
1000 = 5 per cent. fatty acid.		

BRIGHTENING OIL II.

200	grms.	Turkey-red oil 25 per cent.
3	,,	oxalic acid.
2½	,,	tin crystals.
600	,,	water: add ammonia until the precipitate formed is re-dissolved and make up to—
1000 = 5 per cent. fatty acid.		

The cloth (preferably dry) is padded through either of the above solutions, dried, and then steamed in a "cottage" at 5 lbs. pressure for one hour. After washing, the goods are soaped 15–20 minutes at 75° C. in a solution of 3 parts of soap per 1000 of water. If the whites still retain a pinkish tinge, the pieces, after being well washed out of the soap becks, are finally cleared by being passed through a solution of bleaching powder ¼°–½° Tw., steamed wet for a minute, washed, and dried up over cylinders. The *clearing* is effected in the machine already described.



Madder Red (C.P.A.).

The effect of oiling as above is to intensify the depth and increase the brilliancy of the red, while at the same time the oxalic acid liberated in steaming produces a very pure, clear white. The oil combines with the colour lake to form an Alizarin alumina tin fatty compound of extreme fastness to light and soap.

Before the discovery of the soluble oils, the brightening of dyed reds was always done by boiling them with a neutral soap, to which was added a very small percentage of tin crystals. The process was long, and no better than the modern oiling and steaming method.

Madder Orange is produced in exactly the same way as the red, with the sole exception that Alizarin orange is used in place of Alizarin. It is rarely employed alone, being for the most part used in combination with Aniline black. The same printing colour, viz. 6 T. Red, serves for orange, and indeed for all colours dyed on an alumina mordant.

As already mentioned, the name 6 T. Red is merely a convenient expression of the strength of the aluminium acetate printed. Weaker and stronger colours are distinguished in the same way. Thus—

½	T. Red. (aluminium acetate)	½° Tw.	(thickened) gives	Light Pink.
1½	„ „ „	1½° Tw.	„ „	Dark „
6	„ „ „	6° Tw.	„ „	Medium Red.
8	„ „ „	8° Tw.	„ „	Full rich „
12	„ „ „	12° Tw.	„ „	Crimson.

The shade of red produced varies with the shade of Alizarins used in dyeing. Scarlets are dyed with the yellow shades; pinks and crimsons with the blue shades. In the latter cases, too, it is advisable to use a brightening oil without tin, since tin tends to make the shade yellowish and very fiery—a desirable quality in scarlets, but a defect in crimsons and pinks.

In addition to various shades of red, pink, orange, and salmon, the above simple aluminium mordants are all suitable for the production of a great number of yellows, browns, clarets, fawns, olives, etc., all dyed directly on the dunged cloth, and finished off with no further after-treatment than a thorough washing and soaping, with perhaps a run through the chemicking machine to brighten the whites when these have suffered in dyeing from too great an excess of dyestuff, too long an immersion, or too high a temperature. It is important to observe that, in order to preserve the purity of the whites (the unprinted parts of the cloth), the dyeing should always be conducted at as low a temperature as is consistent with the production of a fast colour lake.

The following colours are all suitable for dyeing on aluminium mordants:—

Alizarin bordeaux.	Quercitron bark extract.
„ orange.	Persian berry extract.
„ red, all brands.	Anthracene brown.
„ brown.	Chromophenine F.K.N.
„ blue (in mixtures only).	Logwood (in mixtures).

A fine shade of *claret*, much clearer in tone than can be obtained on any aluminium and iron mixed mordant, can be produced on 8 *T. Red* by dyeing the cloth in a mixture of Alizarin bordeaux and Alizarin (blue shade).

Dye Bath for Claret (100 kilos. cloth).

6 kilos. Alizarin 20 per cent. paste (blue shade).
1½ „ Alizarin bordeaux B.B.D. paste.
¾ „ tannic acid.
10 „ glue size 15 per cent.
1500–2000 litres water.

Dye as for Alizarin red; wash, oil, steam, wash, and soap.

Mixtures of Quercitron bark or Persian berry extracts, with small quantities of Alizarin, Alizarin bordeaux, Anthracene brown, Alizarin orange, give rise to a vast variety of compound shades when dyed on *8 T. Red* mordant. As a rule, however, all compound shades except the most brilliant are dyed on chocolate mordants of various kinds. Chocolate mordants are mixtures of iron and aluminium acetates.

Alkaline Reds, so called, are merely Madder reds, dyed on an alumina mordant, prepared by thickening "alkaline mordant" or *aluminate of soda* ($Al_2O_3.Na_2O$). For fixing the alumina on the fibre, the printed goods are either simply exposed to the action of the atmospheric carbonic acid or passed for from two to four minutes through a solution of sal ammoniac (ammonium chloride), or through a solution of phosphoric acid prepared by the double decomposition of superphosphate of lime and sulphuric acid.

$$(1)\ Na_2Al_2O_4 + CO_2 + 3H_2O = Na_2CO_3 + 2Al(OH)_3.$$
$$(2)\ Na_2Al_2O_4 + 2NH_4Cl + 2H_2O = 2NaCl + 2NH_3 + 2Al(OH)_3.$$

In each case, the precipitation being effected in presence of moisture, the oxide of aluminium is deposited on the fibre as the hydrate. With ammonium chloride care must be taken to avoid an excessive accumulation of ammonia in the bath, since it is liable to dissolve or strip a portion of the alumina from the cloth.

The chloride and sulphate of zinc have been proposed as fixing agents for alkaline red mordant, but, while they answer perfectly for the purpose, they possess no particular advantages over other fixing agents, and, if used at all in practice, they serve merely as alternatives.

Perhaps the best and most reliable fixing agent is that proposed by B. W. Gerland, viz. phosphoric acid. It is very effective, does not strip the fibre of alumina (phosphate of alumina is insoluble), and can be very cheaply prepared from the commercial superphosphate of lime by the action of warm dilute sulphuric acid. The essential constituent of superphosphate is calcium phosphate; sulphuric acid precipitates the calcium as sulphate, leaving phosphoric acid in solution.

$$Ca_3(PO_4)_2 + 3H_2SO_4 = 3CaSO_4 + 2H_3PO_4.$$

The insoluble calcium sulphate is filtered off and the clear filtrate of phosphoric acid reduced with water, as required, to the requisite working strength —about 8° Tw. on the average.

Solutions of alkaline mordant are best thickened with maize starch and a little tragacanth. Wheat starch and flour are both unsuitable, by reason of the fact that they become ropy and gelatinous when treated with strong alkalies.

Well torrefied British gum, *i.e.* dark British gum, is also an excellent thickening agent, but it gives lighter reds than maize starch, and is therefore only useful for pinks.

The following example of the method of producing alkaline red is taken from practice:—

PRINTING COLOUR (10 Alk. Red).

8 parts by weight maize starch.
50 ,, ,, ,, water.

Boil, turn off steam, and add—

2 parts by weight Turkey-red oil.
10 ,, ,, ,, tragacanth thickening 6 per cent.

Cool and add gradually—

30 parts by weight alkaline red mordant 30° Tw.

100

Heat again to 75° C. and then cool.

The above colour corresponds to alkaline mordant at 10° Tw., plus, of course, the thickening.

Print on white, unoiled cloth; dry; hang overnight in a cool, airy hanging room to soften the thickening; and then fix by a two or three minutes' run through either of the following baths:—

Fixing Bath I.—Ammonium chloride solution 10° Tw. at 60° C.

Fixing Bath II.—Phosphoric acid 8°–10° Tw. at 60° C.

The fixing is most conveniently performed in the ordinary fly dunging machine.

After a thorough wash, the fixed pieces are treated exactly like ordinary Madder styles; that is, they are dyed, washed, oiled, dried, steamed, washed, soaped, and (if necessary) lightly cleared in bleaching powder solution.

Cloth mordanted by means of aluminate of soda is identical in its behaviour towards colouring matters with cloth mordanted in the usual way with aluminium acetate and other *acid* aluminium salts.

The great advantages of aluminate of soda as a mordant for printing are, that it will stand drying at a comparatively high temperature without injury; that, owing to its nature, it is not liable to contract iron stains; and that it penetrates well into the fibre, thus yielding good, solid colours, and allowing of *reversible effects* being produced with ease on thin cloth and by ordinary printing on one side. Moreover, the alkaline red process is quicker than the regular Madder process, and for this reason it has largely displaced the latter for the production of red and white prints. On the other hand, aluminate of soda is much more limited in its application than the acetates of alumina, since its alkalinity precludes its association with Aniline black and the iron mordants in direct multicolour patterns. As a resist under Aniline black covers, however, it yields fast red, black and white effects. It is rarely used at the present time for this purpose, other quicker and more modern methods having displaced it.

Madder Chocolates.—These colours are obtained by dyeing Alizarin on a mixed mordant of iron and alumina. They therefore consist essentially of mixtures of Madder red and Madder purple, since the Alizarin iron lake is purple.

According to the proportion of iron in the mordant, Madder chocolates vary in shade from maroon to plum; the smaller the quantity of iron the redder the shade, the greater the quantity of iron the darker and bluer the shade.

For convenience of working, the amount of aluminium acetate (red liquor) taken is generally a simple multiple of the amount of iron liquor (pyrolignite) taken, and this relation is most commonly expressed numerically in the distinctive name given to the colour. Thus:—

		Red Liquor 8° *Tw.*		*Iron Liquor* 24° *Tw.*
8 Chocolate	=	8 parts	and	1 part.
16 ,,		16 ,,	,,	1 ,,
20 ,,		20 ,,	,,	1 ,,
40 ,,		40 ,,	,,	1 ,,
		Etc.		

Lighter shades of these colours are indicated in various ways in different works. The one mentioned, when dealing with the mixing of compound shades, is perhaps as convenient as any. Thus, a colour written "8 Chocolate 2" means that 1 part of 8 Chocolate (see above) is reduced in strength by the addition of 2 parts of starch or flour paste; or is made correspondingly weaker in the first instance. Similarly:—

20 Chocolate $\frac{1}{4}$ = 4 parts of 20 Chocolate and 1 part of paste,
16 ,, 4 = 1 part ,, 16 ,, ,, 4 parts ,,

and so on.

The processes of printing, ageing, dunging, and dyeing Madder chocolates are exactly the same as those for reds. In the oiling, however, tin crystals and oxalic acid are, of course, left out, as they would effect the reduction of the iron mordant, and thus give rise to irregular work.

Some printers prefer to age all goods printed in iron mordants in the old-fashioned hanging rooms, and where these are available it is perhaps the safest method to adopt. The oxidation of the iron requires to be carefully effected, and certainly it can be carried out more evenly and regulated with greater precision in the hanging rooms, where the goods are suspended in single folds, and every part of the cloth is subjected to the same atmospheric conditions of heat and humidity, than when the goods are bundled up and allowed to lie in piles, with only the outer folds of the bundle fully exposed to the action of the air, as is the case when the continuous ageing machines are made use of. If hanging rooms are not available, the goods, after passing through either Crum's machine or the rapid ager, must be piled, as loosely as possible, in small lots, and turned over frequently during a period of two to four days, in order to equalise the oxidation.

The following is an example of a Madder chocolate printing colour largely used in practice for the production of dark shades.

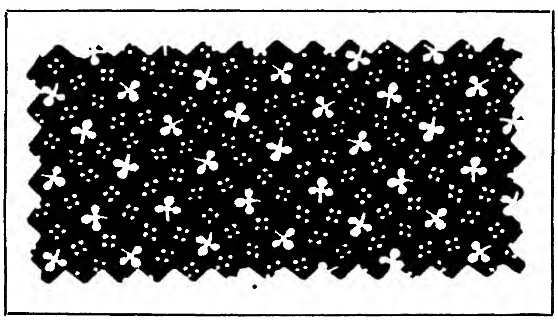
20 Chocolate.

120	parts by weight	of	flour.
40	,,	,,	olive oil.
800	,,	,,	red liquor 8° Tw.
40	,,	,,	iron liquor 24° Tw.
0·5	,,	,,	Magenta (for sightening).
1000			

Boil and cool.

Print on white, unprepared cloth, age, dung, dye, wash, oil, steam, wash, soap, and clear (if necessary) in chemick as for reds.

The strength of the dye bath varies with the amount of mordant printed on the cloth. For an average pattern covering half the cloth about $7\frac{1}{2}$ per cent. of Alizarin on the weight of the cloth would give a full shade on 20 *chocolate*, the other ingredients of the dye bath, glue and chalk, being the same as for reds. It ought to be observed that tannin (sumach) is omitted from chocolate dye baths on account of the black compound it forms with iron salts; it may be replaced, if desired, by bran, but the addition of bran is not necessary, although it tends to preserve the purity of the whites.



Madder Chocolate (C.P.A.).

In addition to Chocolates, many other shades can be dyed on iron-alumina mordants, and in some such cases tannic acid or sumach plays an important part as a dyestuff in modifying the shade of the colour.

Examples :—

(1) Fawn on 12 Chocolate 1.

Dye bath (for 100 kilogrammes cloth printed in a heavy blotch).

1·200 kilos. Alizarin (yellow shade) 20 per cent. paste.
40 „ Persian berry liq. 18° Tw.
6·400 „ dried sumach.
0·275 „ ammonia ·880.
2000 litres water.

Dye for 80 minutes in all,—15 minutes in the cold, 15 minutes at 40° C., 15 minutes at 50°–60° C., and the rest of the time at 75° C. Wash well after dyeing, and then soap at 60° C. for 10 minutes with 2 grammes of soap per litre of water.

(2) Warm Dark Brown on 20 Chocolate.

For 100 kilos. cloth.

3 kilos. Anthracene brown (in paste).
3 „ Alizarin orange 20 per cent.
6 „ 20 per cent. glue solution.
2000 litres water.

Dye, wash, soap, and clear.

(3) Dark Olive on 40 Chocolate.

For 100 kilos. cloth.

8 kilos. Alizarin orange 15 per cent.
6 „ sumach powder.
6 „ 20 per cent. glue solution.
2000 litres water.

Dye, well wash, and then re-dye in—

2½ kilos. Methylene green (extra yellow).
½ „ Auramine O.
15 „ alum.
¼ „ sulphuric acid 168° Tw.
1500 litres water.

Dye at 50° C., wash well, treat 15 minutes in an infusion of bran at 80° C., wash well, soap, wash, and clear. The addition of alum and sulphuric acid aids in keeping the whites clean. Alizarin itself acts as a mordant for basic colours, but for fast colours it is always advisable to use tannin matters along with it, since they form much more insoluble lakes with the basic dyestuffs applied in the second dyeing, or " topping " as it is termed technically.

Many of the Chrome or Mordant colours used in direct printing dye up excellently on madder mordants, especially on chocolate mordants. The colours produced are, perhaps, not quite so fast to soaping as those obtained on chromium mordants, but they fulfil all reasonable requirements, and, from a practical point of view, they are more convenient to handle in works where a large amount of madder work is done, because, up to the stage of dyeing, they conform to routine processes. Furthermore, in resist styles, it is much easier, on madder mordants than on chrome mordants, to counteract the effects of the smearing or *scumming* of the resist during printing—a defect very liable to occur in this class of work,—and on the whole more consistent results are obtained in dyeing.

One instance will suffice to illustrate this method of applying Chrome colours—a method largely employed for the production of rich, full navy blues.

NAVY BLUE ON 40 CHOCOLATE (padded).

Dye (for 100 lbs. cloth).

10 kilos. ground sumach.
6 „ 20 per cent. glue solution.
1 kilo. chalk.
2000 litres water.

After dyeing, wash well and re-dye in—

5 kilos. Chromophenine F.K.N.
6 „ 20 per cent. glue solution.
2000 litres water.

Dye 1 hour, raising the temperature gradually to 75°–80° C., and continue dyeing for 15–20 minutes. Wash well and clear as usual by a run through the chemicking machine.

Blacker shades of blue may be obtained by the addition of a small quantity of Quercitron bark to either the first or second dyeings; and similarly brighter and more lively shades are obtained by adding suitable basic blues, greens, or violets to the second dye bath.

By this method also are applicable: Modern violet, Modern blue C.V.I., Modern yellow, Ultra violets, Anthracene blues, and many other mordant colours, all of which may be mixed together, or with Alizarins, in any proportion to form compound shades. The navy blue style is the most important.

The foregoing examples of compound shades will show that the Madder style is capable of a good deal of variation. Many other instances could be given, but they would be simply repetitions of the above with different dye-stuffs, and as such would only take up space without affording any corresponding advantage.

Madder Purples.—The production of Madder purples is strictly analogous to that of all other Madder colours; but, unless in combination with red, they are never oiled and steamed, the clearing of the whites and the brightening of the colour being effected by repeated soapings at the boil, varied occasionally by a treatment in bran or in chemick.

Madder purples and Madder blacks are both obtained by dyeing Alizarin on iron mordants; in fact, the only real difference between them is that in blacks the iron mordant used is many times stronger than in purples; so that, in the abstract, a Madder black is, to all intents and purposes, an intense purple, so dark as to appear black by comparison. When placed side by side with an Aniline or a Logwood black, however, its purple tone is at once apparent.

The iron mordant used for purples is the pyrolignite of iron already described. To this is usually added a certain proportion of arsenious oxide, the object being to retard the rate of oxidation. The arsenious oxide (As_2O_3) is introduced in various ways: (1) by boiling it up with iron liquor; (2) in the form of a solution in water, glycerine, or acetic acid and ammonium chloride; and (3) by preparing the cloth in a weak aqueous solution before printing. All such solutions are known as *purple fixing liquors*, and their composition is, within limits, so much a matter of fancy that probably no two printers use the same formula.

Gros-Renaud in his work on mordants in dyeing and printing[1] states that arsenite of soda may be used, with good results, as a " fixing liquor " for iron mordants. Such may well be the case, but the salt is almost unknown in this connection and certainly possesses no advantage over the usual preparations of arsenious acid cited above.

[1] *Des Mordants en Teinture et en Impression*, Masson et Cie, Paris, 1898.

Depierre gives the following as a suitable preparation of iron for dyed purples:—

$\begin{cases} \text{100 litres iron liquor 24° Tw. (pyrolignite).} \\ \text{1 kilo. white arsenic } (As_2O_3). \end{cases}$

Boil ½ hour, settle, and decant the clear liquor for use.

A separate fixing liquor for adding to the iron liquor during the boiling of the printing paste is made up as under. It has been used with success for a long number of years on the large scale.

Purple Fixing Liquor.

80 litres water.
20 ,, acetic acid 9° Tw.
10 kilos. sal ammoniac (NH_4Cl).
10 ,, arsenious oxide.

Boil until dissolved; then allow to settle, and decant the clear solution for use.

The solution used for preparing the cloth before printing is as follows:—

M. Prepare.

3-	5	grms.	arsenious oxide.
3-	5	,,	sodium chlorate.
994-	990	,,	water.
1000	1000		

The object of the sodium chlorate is to form arsenate of iron during the ageing,—a salt which oxidises very slowly, and is not liable to oxidise beyond the point required to yield the best results on dyeing. The same prepare is sometimes used for chocolate mordants with the same end in view. If the purple printing colour itself contains arsenious acid, the preparation of the cloth is restricted to the application of sodium chlorate alone.

Whether the employment of arsenical fixing liquors and chlorate of soda, with or without the addition of ammonium chloride, common salt, or glycerin, is absolutely essential to the production of the best Madder purples, has never yet been definitely ascertained. Some calico printers have maintained that all such additions are superfluous, while others have been equally emphatic to the contrary. The whole question is probably one of plant and process more than of anything else. In works where the ageing arrangements are particularly favourable to the slow and gentle oxidation of the iron mordants, it may be easily possible to obtain first-class work without the assistance of any fixing liquors in the printing colours; and in such cases it would be manifestly absurd to increase the cost of production by making useless additions. On the other hand, most calico printers bear witness to the value of arsenious oxide in promoting regular work; and, taken altogether, the balance of evidence seems to be in favour of employing it, either alone or in combination with glycerin, ammonium chloride, or common salt, and sometimes chlorate of soda or potash.

The thickening used for Madder purples may be either flour, starch, or British gum—the last usually for a variation of the Madder style known as the "cover and pad style," which will be dealt with later. "Paste purples" (P. purples) give shades almost as dark again as "Gum purples," the strength of the mordant being the same in both instances. This is, of course, on a par with what occurs with all classes of colouring matters, but it must be borne in mind when it is necessary to change the thickening for any technical reason.

The nomenclature of Madder purples is similar to that of the chocolates, with this difference, that the figure in front of the name indicates the volume

of water taken to dilute one volume of pyrolignite of iron standing at 24° Tw. Thus—

12 P. purple	=	12 vols. of water to 1 vol. iron liquor 24° Tw.	or	12 : 1
40 ,,	=	40 ,, ,,	,,	40 : 1
240 ,,	=	240 ,, ,,	,,	240 : 1

The letter P. denotes that the solution is thickened with starch or flour; G. would indicate British gum. Any other distinctive signs such as S., F., or BG., etc., might be used as agreed upon. The name of the colour is immaterial so long as its signification is understood.

Apart from the employment of arsenical fixing liquors, the preliminary preparation of the cloth, and the omission of the oiling process, the *modus operandi* of purple dyeing is practically that of Madder reds and chocolates.

The following formulæ will illustrate the method of boiling Madder purple printing colours.

20 P. PURPLE (Medium).

200 litres water.
10 ,, iron liquor 24° Tw. containing 1 per cent. As_2O_3.
26 kilos. flour.
3 ,, olive oil.
0·1 ,, Methyl violet (for sightening).

Boil and cool.

200 P. PURPLE (Pale Lavender).

200 litres water.
1 ,, iron liquor 24° Tw.
¼ ,, fixing liquor. (See page 462).
25 kilos. flour.
2½ ,, olive oil.
0·1 ,, Methyl violet.

Boil and cool.

Print both the above on white cloth prepared in a solution of 3 grammes chlorate of soda per litre; dry, age, dung twice; wash, dye in Alizarin (blue shade); wash well; bran for 15 minutes at 90° C.; wash well, and then soap at 90°–100° C. for 15 minutes, or until the whites are clean. Finally, if necessary, clear lightly in bleaching powder.

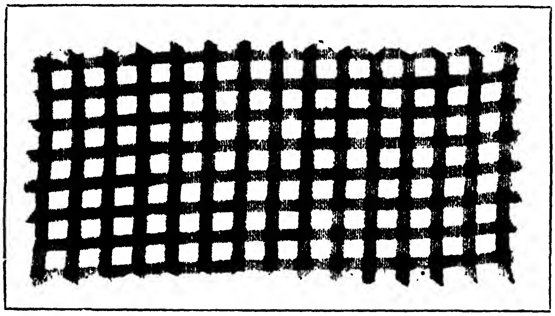
For 20 P. purple (a heavy pattern) the following dye bath will yield a fully dyed shade on 100 kilos. of cloth :—

3 kilos. Alizarin blue shade 20 per cent.
6 ,, glue size 25 per cent.
¼ kilo. chalk (if necessary).
2000 litres water.

Weaker shades of purple require weaker dye baths; but the dye bath ought not to be *too dilute*, otherwise the dyeing will take too long. On the contrary, too great an excess of Alizarin will inevitably stain the whites badly, making it impossible to clear them properly without impoverishing the colour.

Modern Madder purples are in general of a brighter and livelier shade than those dyed before the introduction of the coal-tar colours. This is due not merely to the use of artificial Alizarin, which is free from the brown colouring matters contained by the madder root, but also, and mainly, to the almost universal practice of topping Madder purples with Methyl violet. The Alizarin

acts as a mordant for the basic violet, and the resulting compound shade is much purer and brighter than the simple Alizarin iron lake. Topped purples are fairly fast to soap, but the basic colour soon fades when exposed to light, leaving the original Madder purple somewhat less bright than it was before topping. On the whole, therefore, the topping of dyed purples is more in the nature of an expedient to enhance the appearance of the goods temporarily than of a permanent improvement in the quality of the colour.



Madder Purple (C.P.A.).

The topping is done, after the dyed goods have been well soaped and washed to clear the whites, in solutions of Methyl violet, varying in strength from $\frac{1}{16}$ to $\frac{1}{4}$ per cent. of dyestuff, reckoned on the weight of the goods, and according both to the depth of the purple to be treated and the shade desired. It is usually performed at about 40°–45° C., and a little acetic acid is generally added to the bath to preserve the purity of the white parts of the cloth. Care must be taken to avoid any excess of acid, otherwise the tone of the Madder purple will be changed to an unpleasant yellowish-grey. After topping, the goods are again well washed in warm water, lightly soaped, and finally well washed and dried. An alternative method is to add the Methyl violet to the Alizarin in the dye bath in the first instance and dispense with topping.

Madder Black.—Blacks dyed with Alizarin on an iron mordant are only employed in combination with dyed reds, chocolates, and purples; and even for this purpose they have been almost entirely superseded by Aniline blacks, which yield a much finer shade and give a very much sharper impression of the pattern. Still Madder blacks do find occasional use in some styles, and, apart from other considerations, any mention of the Madder style would be incomplete without some note on the methods of obtaining a black, along with other colours, by dyeing.

For small objects on lightly engraved rollers the strength of iron liquor required to give a black on dyeing in Alizarin is from 12°–16° Tw.; heavier patterns often yield good results with 6°–8° Tw.

12° T. Black.

45	litres	iron liquor 24° Tw.
35	,,	water.
10	,,	purple fixing liquor. (See page 462).
10	kilos.	flour.
$2\frac{1}{2}$	,,	British gum.
$2\frac{1}{2}$	,,	olive oil.

Boil and cool. Sighten with Logwood.

Logwood is sometimes added to the above to intensify and modify the shade.

Print on cloth prepared in chlorate of soda as under:—

M. Prepare.

5	grms.	chlorate of soda.
1000	,,	water.

Dry; age by hanging 4 days at 30° C. dry bulb, 27° C. wet bulb, or through the rapid ager as already described; dung; wash and dye in any dye bath suitable for the other colours printed in the combination; wash, soap, and clear.

Resorcin Green.—If dinitroso-resorcin be substituted for Alizarin in the dyeing of any of the foregoing Madder purple (iron) mordants, green shades, of great fastness to light and soap, are obtained. These shades vary from deep myrtle to the palest of sage greens, and are usually known as Resorcin or Alsace greens.

Multicolour Patterns in the Madder Style.

The Madder style, pure and simple, does not allow of much variety being obtained in the way of colour combinations. At most it is only possible to produce, *by dyeing*, combinations of four types of colour, *e.g.* red, chocolate, purple, and black, but it so happens that Catechu and lead sulphate can be fixed on the cloth sufficiently permanently to withstand all the operations connected with the dyeing and clearing of Madder colours. This fact permits of Catechu brown and Chrome yellow or orange being associated with any of the dyed colours already mentioned, so that it is possible to obtain combinations of six different classes of colours in the Madder style by a few simple modifications of process. Catechu and Chrome yellows used in this connection are generally known as "Madder brown" and "Madder yellow" respectively —a terminology not quite correct, but one readily understood under the circumstances.

Patterns containing Chrome yellow are always printed on cloth prepared in sodium sulphate, with the obvious object of precipitating insoluble lead sulphate in the fibres of the material. This lead sulphate withstands all the operations of dyeing, etc., and is finally converted into Chrome yellow by a treatment in bichromate of potash.

The introduction of Catechu makes it necessary to age the goods for from four to six days in a warm, moist atmosphere, and in hanging rooms where a good circulation of air can be maintained. The fixation of Catechu is effected by a process of oxidation, and if this is incomplete the resulting colour is correspondingly loose and washes off in dyeing. Similar conditions of ageing are suitable, and safest, for sulphide and vanadium Aniline blacks, and are, likewise, the best for aluminium and iron mordants. Simple air oxidation, however prolonged, does not develop the colour of Catechu to anything like the same extent as bichromate of potash does; hence Catechu browns in the Madder dyed styles are always rather light in shade, the use of bichromate of potash before dyeing being inadmissible. The presence of copper salts and ammonium chloride promotes a more complete oxidation; and the shade is also intensified by the addition of red liquor, which, by attracting colour from the dye bath, makes it darker, and at the same time rather redder in tone.

CATECHU MADDER BROWNS.	I.	II.
Catechu, 25 per cent. solution	65 litres.	65 litres.
Water	9 ,,	4 ,,
Starch	10 kilos.	10 kilos.
Gum tragacanth, 6 per cent.	8 litres.	8 litres.
Ammonium chloride	3 kilos.	3 kilos.
Olive oil	3 ,,	3 ,,
Boil, cool, and add—		
Nitrate of copper 80° Tw.	4 litres.	4 litres.
Red liquor 8° Tw.	none.	5 ,,

Catechu Solution, 25 per cent.

25 kilos. Catechu in cubes.
40 „ water.
35 „ acetic acid 9° Tw.

Boil 6 hours, make up to the original volume, stir well, and allow to settle for from 24 to 36 hours. Then decant the supernatant liquor for use as above; or the liquor may be thickened with gum Senegal 4 lbs. per gallon, in which case a printing colour can be made by adding copper nitrate, ammonium chloride, and a little reduction, thus:—

60 litres thickened Catechu solution 25 per cent.
5 „ nitrate of copper 80° Tw.
5 „ gum Senegal solution 60 per cent.
5 kilos. ammonium chloride.

For Madder yellows the best salt to use is a basic lead acetate made by boiling the normal acetate with litharge. Thus—

9 litres water.
6 kilos. lead acetate.
2¼ „ litharge.

Boil one hour; replace the evaporated water; settle and filter.

Lead or Madder Yellow.

100 litres basic acetate of lead as above.
25 kilos. light British gum,
or
40 kilos. powdered gum Senegal.

Heat till dissolved, and then cool.

The rollers used for printing Catechu browns and lead yellows in the dyed Madder styles ought to be strongly engraved in order to transfer a heavy charge of colour to the cloth, and thereby compensate for the loss of depth which these colours are apt to suffer during the long series of severe operations that are essential to the dyeing and clearing of the Alizarin colours.

The following is a summary of the various stages in the production of a six-colour print in red, yellow, brown, purple, chocolate, and black:—

(*a*) Preparation of the Cloth.—Slop-pad in a mangle through—

250 grms. sulphate of soda.
50 „ chlorate of soda.
10 litres water.

Dry over steam-heated cylinders.

(*b*) Printing.—On the prepared cloth print a six-colour pattern in—

(1) Madder yellow as above.
(2) 8 T. red (Madder red).
(3) Catechu Madder brown I.
(4) 20 Chocolate ½ (Madder chocolate).
(5) 20 P. purple (Madder purple).
(6) 16 T. black (Madder black), or a Sulphide Aniline black.

(*c*) Ageing.—Pass through Crum's continuous ageing chamber for 20 minutes at 32° C. dry-bulb, 28° C. wet-bulb thermometers, and then hang three to four days under similar conditions of heat and humidity. During this latter part of the ageing process the Catechu browns and the Aniline black (if any) are oxidised and developed as far as is possible at this stage.

(*d*) DUNGING.—After ageing, the printed pieces are dunged as usual, but without cow-dung when yellows are present.

First dunging for 3 minutes at 60° C. :—

10 kilos. phosphate of soda,
10 „ chalk,
200 „ sulphate of soda,
1000 litres of water,

in the continuous fly dunging machine. Wash and dung a second time in—

2½ kilos. phosphate of soda,
2½ „ chalk,
100 „ sulphate of soda,
1000 litres of water,

for half an hour at 50°–60° C., in the spiral becks. Wash well and dye.

(*e*) DYEING.—For a fairly heavy sprig or spray pattern take for the dye bath per 100 kilos. of cloth—

3–4 kilos. Alizarin 20 per cent. paste.
4 „ glue size 25 per cent.
½ „ chalk.
4 „ bran (optional).
2000–2500 litres of water.

Dye ¼ hour in the cold, then gradually raise the temperature during the course of ¾ hour to 70°–75° C., at which temperature continue the dyeing for ½ hour. Then bran ¼ hour; wash and clear.

(*f*) CLEARING.[1]—Treat the washed goods for 10 minutes at 50° C. in—

(1) 1200 litres water.
2 „ bleaching-powder solution 8° Tw.
2 „ soda-ash solution 8° Tw.

(2) Wash, soap ½ hour at 90° C. with 2 grms. soap per litre. Wash well.
(3) Repeat operations (1) and (2).
(4) „ „ „
(5) Wash again and then raise the Chrome yellow or orange.
(6) RAISING: Treat the goods for 10 minutes at 60° C. in—

1000 litres water.
5 kilos. bichromate of soda.
2½ „ sulphuric acid 168° Tw.

Wash well; and then, if an orange is required, pass the goods into a warm solution of the following:—

1000 litres water.
1 kilo. bichromate of soda.
1 „ quick lime.

Treat for about 10 minutes at 30°–40° C.; then wash well and soap.

These multicolour patterns produced by dyeing are very fast, but they are not particularly bright, and their cost of production is very high compared with that of similar work executed by direct printing in colours developed by steaming.

FURNITURE AND UPHOLSTERY GOODS.—A style largely employed in the furnishing trade consists of a heavy repp cloth printed " en camaïeux " in different shades of red. The patterns mostly used for this purpose are Renaissance scrolls, rococo designs, and large stripes, either plain or fancy; they cover

[1] If desired, the clearing may be equally well done on an ordinary clearing or chemicking machine (*q.v.*).

the whole surface of the cloth, not a vestige of white being left. This allows of the mordants being printed on *oiled cloth.* In all Madder styles containing white objects or spaces in the pattern, the use of Turkey-red oil *before dyeing* is altogether inadmissible, since it attracts a certain amount of colour from the dye bath to the white unprinted parts of the cloth, and this colour adheres so obstinately to those parts that it is practically impossible to remove it, except at the cost of impoverishing the brilliancy and strength of the colours on the mordanted parts. This defect, however, becomes an advantage in patterns on a red, pink, or any other colour of a Madder-dyed ground, because the presence of an insoluble oil alumina mordant not only gives the brightest shades, but it also admits of the goods being treated by a process closely approximating to the dyeing of Turkey red, which is by far the fastest and most brilliant of all the colours derived from Alizarin.

The majority of such patterns used for furniture, etc., consists of four colours—chocolate, dark red, light red, and pink. The first three of these are printed in the ordinary way on the printing machine or by hand block; the last is applied by slop-padding the goods in a weak mordant after the printed mordants have been aged and dunged. The weaker or pink mordant may be applied before printing and immediately after oiling the cloth, if desired, but in practice the best results have been obtained by operating in the way described. The ageing and dunging are then repeated to fix the pink mordant, after which the dyeing is proceeded with in exactly the same manner as for ordinary Madder reds. Oiling in Turkey-red oil and steaming under pressure follow the dyeing; and finally, the colours are specially brightened by a treatment in dilute mineral acid and, after washing, in soda chemick.

The preliminary preparing of the cloth in oil is effected in a padding mangle with a large trough or beck, the object being thoroughly to saturate the cloth. The drying is done over steam-heated copper cylinders. The cloth employed is bleached as for Turkey reds; that is, it is simply boiled two or three times in caustic soda, and then washed, soured, washed, and dried without any treatment in bleaching powder. A synopsis of a process largely used in practice for the production of a "Chocolate, red and pink" effect is given below.

1*st operation.*—Pad the cloth in a 5 per cent. solution of olive oil oleine and dry over copper cylinders.

2*nd operation.*—Repeat operation 1, dry and stove in hanging room at 75° C.

3*rd operation.*—Pass through a solution of soda ash 1½° Tw. and wash.

4*th operation.*—Repeat operations 2 and 3.

5*th operation.*—Steam the goods in bundles for 1 hour at 4 lbs. pressure, then allow them to lie in pile in a warm room for two days.

6*th operation.*—Print for the Chocolate :—10 Chocolate.
,, ,, Dark red :—14 T. Red.
,, ,, Light red :—4 T. Red.

7*th operation.*—Age in any of the ways already described, but preferably by hanging 2–4 days in a chamber heated to 36° C., and containing moisture equal to 32° C. wet-bulb thermometer.

8*th operation.*—Fix in a continuous fly dung machine in—

4000 litres water.
60 ,, binarsenate of soda 18° Tw.
20 ,, cow-dung.
2 kilos. chalk.

Pass the goods in the open width through the above at 60° C., and at such a speed that the treatment occupies 4 minutes. Then wash and dung in—

$$\left\{\begin{array}{lll}4000 & \text{litres} & \text{water,} \\ 20 & ,, & \text{binarsenate of soda } 18° \text{ Tw.,} \\ 30 & ,, & \text{cow-dung,}\end{array}\right.$$

at 40° C. for from ½ hour to 20 minutes. Wash well in spiral becks and dry over copper cylinders.

9*th operation.*—Pad the dried goods in the open width through a solution of red liquor ½° Tw.; dry.

10*th operation.*—Age through Crum's machine at 32° C., allow to lie overnight in loose pile, and then fix again through the first dunging liquor given in operation 8. Wash well and dye.

11*th operation.*—Dyeing.—Dye with 10 per cent. Alizarin 20 per cent. paste (blue shade), 3 per cent. sumach, 1 per cent. chalk, 2½ per cent. Turkey-red oil, 3 per cent. glue size 25 per cent., and a sufficiency of water. Dye ¼ hour in the cold; then raise the temperature gradually in ¾ hour to 80° C., and dye at that for ½ hour or longer. Wash well, hydro-extract the goods, and then open them out to the full width, and, without drying them, proceed to the next operation.

12*th operation.*—Preparing.—Pad the goods in a 5 per cent. solution of Turkey-red oil, and dry them over cylinders.

13*th operation.*—Steam the dry oiled pieces for an hour at 5 lbs. pressure. Wash well and soap.

14*th operation.*—Soap at the boil for ½ hour. Wash well.

15*th operation.*—Soap at the boil for ½ hour. Wash well.

16*th operation.*—Pass for 2 minutes through hydrochloric acid ¾° Tw.

17*th operation.*—Wash well and pass for 4 minutes through a solution of soda chemick 2°–3° Tw. Wash well and dry.

Operations 16 and 17 are carried out in continuous machines, as the cloth must not be allowed to lie after its treatment in acid and soda chemick solutions, either of which would rapidly destroy the light red and the pink. As a matter of fact, these two operations are only performed when the very brightest colours are demanded.

Various shades of maroon and claret reds are obtained in the above manner by applying mixed iron and alumina mordants to the oiled cloth, and afterwards dyeing in Alizarin. After dyeing, the goods are treated as described up to the 14th and 15th operations.

Certain shades of brown, olive, old gold, fawn, and blue are also produced in the same way by replacing Alizarin with any other members of the group of mordant colours that will dye up on iron and alumina mordants. Thus it is possible to obtain quite a series of fast shades by simply varying either the mordant or the dyestuff as the case may be, the process remaining the same in its main features. For colours other than Alizarin reds, one oiling of the cloth before dyeing is usually enough, or it may be dispensed with altogether in some cases.

Brown effects are obtained either by mixtures of Persian berry or Quercitron bark extracts and Alizarin, or from Anthracene brown, and other shades by suitable mixtures of these with Gallocyanine, Cœruleïn, Galleïn, and Alizarin orange, etc. Some of these "fancy" colours are dyed as under:—

BROWN I.— (Fawn)	$1\frac{1}{2}$	per cent.	Alizarin 20 per cent. paste	Alumina mordants.
	35	,,	Quercitron bark extract 48° Tw.	
	$\frac{1}{2}$	,,	Gallocyanine paste	
BROWN II.—	6	,,	Alizarin orange 20 per cent.	Alumina or Chocolate mordants.
	4	,,	Anthracene brown 30 per cent.	
PURPLE.—	20	,,	Galleïn paste 10 per cent.	Alumina or Iron mordants.
OLIVE I.—	10	,,	Cœruleïn S. 20 per cent. paste	Alumina mordants are the best.
OLIVE II.—	30	,,	Persian berry extract 48° Tw.	
	5	,,	Cœruleïn S. 20 per cent. paste	
OLD GOLD.—	40	,,	Persian berry extract 48° Tw. on 20 Chocolate and its reductions.	

After dyeing, the above shades only require a good washing and soaping for the completion of the process; no oiling or steaming is necessary.

Except for the best quality of goods, and then almost exclusively for reds, the above method of producing the so-called "cameo" effects in three or four shades of one colour has been superseded by the more rapid method of direct printing, or the steam style of printing. The best modern steam colours are little, if at all, inferior in fastness to most of the *fancy* dyed colours, and they possess the immense advantage of being easily and rapidly corrected for shade if they are "off colour." Moreover, the steam style affords greater scope to the colourist in the harmonising of his colour scheme, since it permits him to introduce gradations of tone as well as gradations of shade, and that, too, with the most delicate of colours—a facility not afforded by the Madder style, in which gradations of tone are dependent on the variation of the iron content of the mixed mordants, and consequently are limited to the greater or less dulling of a particular colour. Increase in the proportion of iron means the flattening of all compound Madder colours by the introduction of black (or what comes to practically the same thing, of purple), so that it is impossible to obtain gradations such as result from varying the proportions of the members of a series of colours, like those already dealt with when speaking of the mixing of compound shades.

Dyed Madder Colours and Steam Colours.

In connection with the Madder style, it must be mentioned that certain steam colours are capable of being combined with aluminium and iron mordants in the production of multicolour effects, of which the red, chocolate, and purple are obtained in the Alizarin dye bath in the usual way. The only steam colour that is used to any extent for this purpose is *Alizarin blue.* With very few exceptions, the mordant colours require prolonged steaming for their proper fixation, and are therefore unsuited for use along with red and iron liquors. But Alizarin blue and one or two other blues of the same group (also Chrome violet blue) can be very well fixed, with a chromium mordant, by running twice through a rapid ager. This short steaming does not harm the iron and aluminium mordants, and it fixes the blue so well that it resists the action of the dye bath perfectly. After steaming, the goods are treated exactly as described for ordinary Madder colours. Aniline black can, of course, be added to the combination—also Catechu brown and lead yellow.

Example.—Print a seven-colour pattern in the following colours:—6 T. Red, 12 Chocolate, 20 P. Purple, Catechu Madder brown, Madder yellow (lead), Aniline black (prussiate), and Alizarin blue.

Alizarin Blue for Madder work.

60	grms.	Alizarin blue S.
790	,,	Starch-tragacanth thickening.
150	,,	acetate of chrome 25° Tw.
1000		

Print on cloth prepared with 4 oz. sodium sulphate and ½ oz. chlorate of soda per gallon; pass twice through the rapid ager; allow to lie or to hang a day or two, to age the red, chocolate and purple mordants and the brown; and then dung and dye in Alizarin according to the instructions already given for Madder styles containing lead yellow. After dyeing, wash and bran the pieces for half an hour at 50°–60° C. to clear the white; wash again and develop the yellow in a warm ½ per cent. solution of bichromate of potash. Then wash again and soap at 60° C.

In working this style, care must be taken to avoid an excess of chromium mordant in the blue, otherwise the blue will be converted into a dirty blackish purple during the operation of dyeing. The excess of mordant becomes fixed on the fibre and attracts Alizarin from the dye bath, so that the resulting colour is a mixture of Alizarin blue and Alizarin claret (the Chrome-Alizarin lake).

In order, too, to keep the white parts of the cloth as clean as possible, and to facilitate their subsequent clearing, the dye bath should contain no more Alizarin than is absolutely necessary for the production of full shades of red, chocolate and purple; and the dyeing should be conducted at not above 50° C. until the bath is almost exhausted, at which point the temperature may be raised to 75°–80° C. Alizarin blue is very susceptible to the action of chlorine, and therefore the clearing of the white must be performed almost wholly with bran and soap. A *very light* chloring afterwards may be given if the white is not passable, but it is a risky operation, unless the blue is very dark.

Dark blue, orange, and white patterns for the East are obtained in a similar way by dyeing Alizarin orange on a red mordant printed in combination with Alizarin blue. Phenocyanine blues and Cœruleïn olive have also been used along with dyed Madder colours, in imitation of some of the Battick styles.

Batticking proper is a resist process practised by the Javanese and others, and will be touched upon later. But certain other goods, also produced in Java, have been called battick, and have been imitated more or less successfully by means of the Madder dyeing process combined with Aniline black and Alizarin blue. In this class of work a dark blue is often found in combination with a black or chocolate, and the peculiarity of this black or chocolate is, that it is entirely surrounded by a soft, "fuzzy" outline of red or orange. This characteristic outline has the appearance of having been produced by the spreading of some constituent of the principal colour beyond its proper limits; indeed, it is very similar to the defect known as "bleeding," and the colours used in Europe to imitate it are called technically "bleeding blacks and chocolates."

These Blacks and Chocolates consist of mixtures, in various proportions, of Aniline black and red liquor. In practice a mixture of prussiate and sulphocyanide of copper Aniline blacks have been found to give excellent results, but other Aniline blacks are also suitable.

Bleeding Black.

$\left\{\begin{array}{l}\text{2 parts Aniline black (prussiate).}\\ \text{2 ,, Aniline black (sulphocyanide of copper).}\end{array}\right.$

1 part red liquor.

Chocolate.

2 parts above mixed black.

1 part red liquor, slightly thickened.

These colours are printed along with Alizarin blue and ordinary Aniline black in a two- or three-colour pattern on the printing machine or by block. The goods are then run quickly through damp steam in a long rapid ager to develop the black, and are afterwards allowed to lie overnight in a cool place, so as not to dry too much. In the morning they are padded with a sloppy paste of acetic acid, and are dried very slowly at a low heat. The roller used must be a heavy pad, in order to saturate the cloth thoroughly with acid. The effect of this padding is to dissolve any basic salt of aluminium that may have been formed in the ageing of the black part of the colour; but its main purpose is to cause the red liquor thus re-dissolved to spread or bleed beyond the space occupied by the now insoluble Aniline black. If the first padding does not do this effectually the cloth is padded again. The extent to which the black has bled may be tested by dunging and dyeing a small fent in Alizarin. When satisfactory, the goods are aged, dunged, and dyed as usual for the Madder styles. Alizarin gives a black or chocolate with a red edge; Alizarin orange gives black or brown with an orange edge, and other dyestuffs give edges corresponding to the colour of their aluminium lakes.

A good black with a strong red edge or outline is not easy to obtain, nor are the Chocolates very regular in shade; but as the whole process is intended to imitate native hand work, these irregularities are not very serious defects, unless they are too pronounced.

Cover and Pad Style.—This important and extensively practised variation from the ordinary Madder style is based upon the solubility of iron and aluminium oxides in solutions of citric and tartaric acids, and of citrates and tartrates; in other words, the presence of these solvents prevents the precipitation of iron and aluminium oxides, hydrates, and basic salts on the fibre, and consequently renders impossible their fixation on the cloth as mordants.

In the practical application of the solvent properties of the above-mentioned substances to the production of white patterns on a dyed ground, a thickened solution of any one of them, say citrate of soda, is first printed on white cloth in any desired pattern. The cloth is then well dried and re-printed with a thickened aluminium or iron mordant in the usual way, in either a fine all-over design or a uniform flat ground, covering the entire surface of one side of the cloth.

Wherever the citrate of soda falls under the over-printed mordant the fixation of this latter on the cloth is prevented, with the result that during the operation of dunging it is washed out entirely from those parts of the cloth to which the citrate has been applied; so that on dyeing in Alizarin, etc., a white pattern on a plain or figured coloured ground is obtained,—a pattern corresponding, of course, to that first printed in citrate of soda.

If, in the second or over-printing, a fine all-over pattern is applied, the cloth is said to be "covered," and the roller used is known as a *covering roller or cover*, whereas when a plain uniform ground is printed, the cloth is said to be "padded," the roller employed being called a *pad roller* or a *pad*. An ordinary pad is simply a copper roller engraved over its entire surface with a series of oblique and closely set furrows or lines; a *pin pad* is also engraved evenly over its whole surface, but with minute dots instead of furrows. Both are used for the same purpose, and generally in sequence, with the object of producing a fuller and more even grounding.

A white pattern on a figured background of two different shades of the same or two different colours is obtained by first of all printing the desired pattern in an acid or a citrate; then (*a*) covering in, say, a dark purple, and finally padding in a lighter purple; (*b*)—for a red and chocolate background—covering in a red liquor containing a sufficient quantity of tin crystals ($SnCl_2$) to prevent

the fixation of the iron contained by the Chocolate mordant subsequently padded over it; and (*c*), for a red and purple background, covering in the same resist red liquor, followed by padding in weak iron liquor. The operations of ageing, dunging, and dyeing in each of these cases are identical with those already given in the description of the ordinary Madder style.

Thickened solutions of citrates, tartrates, citric acid, and tartaric acid all go under the general name of "acids."

They are also described as *resists* or *discharges* according to whether they are applied to the cloth before or after the mordants.

Stannous chloride (tin crystals) acts as an efficient resist for iron mordants, but in this connection it is only used along with acetate of alumina for resist reds, since the citrates, etc., give much better and cleaner whites. As a matter of fact, a certain amount of tin is fixed on the fibre, and this, while adding brilliancy to the dyed red, would detract from the purity of the white, because tin is itself a mordant for Alizarin. The Alizarin tin lake is a bright orange.

Citric acid and the citrates are by far the most commonly employed resists for all classes of Madder work. They are very effective in all respects, but being exceedingly hygroscopic they absorb a large amount of moisture during the ageing process, and are apt to spread into the surrounding parts of the cloth by capillary attraction. This defect, known variously as "swelling," "bleeding," "spewing," etc., is particularly liable to occur if they are too strong for the mordant employed, or if the goods are allowed to get too damp in the ageing chambers. To some extent it can be remedied by the addition of China clay to the printing paste, and by making the latter as thick as is consistent with good printing qualities, but it is always liable to occur under any conditions if the resist is too concentrated for the work it has to do.

Tartaric acid and the tartrates are less apt to swell than the citrates and citric acid. They are excellent resists, and for Madder purples tartaric acid is perhaps the best acid to use, although citrate of soda, citrate of chromium, tartrates of soda, tartrate of chromium and citric acid are all employed with success for this purpose by different firms. Tartrate of chromium is employed largely on the Continent as a resist under all Madder mordants except the strongest, such as 14 T. Red, 18 T. Black, and other colours previously given.

Its chief advantage is that it swells very little, and can therefore be used without China clay, which tends to fill up the lines of the engraving.

For very strong alumina and iron mordants it is often necessary to add a small quantity of sulphuric acid, in the form of bisulphate of soda ($NaHSO_4$), to the citric acid and the citrate resists for the purpose of procuring a pure well-cut white. Oxalic acid is also used to the same end, but in both cases ageing in the rapid ager must be avoided if possible, as oxalic and the mineral acids attack the fibre, and, at a high temperature and under the influence of steam, tender it rapidly.

The strength of the simple citric and tartaric acid resists is usually expressed in percentages or in grammes per litre.

Thus 5 per cent. = 50 grms. per litre.

Other resists, being somewhat more complex, are named in the same way as reductions of ordinary colours. Thus an acid marked, say, "M. acid 2/3" consists of two parts of gum or starch paste and three parts of standard "M. acid."

In the following recipes will be found formulæ representative of most of the acids and resists in general use for Madder colours:—

5 per cent. T. Acid.

1 litre British gum solution.
50 grms. tartaric acid.

5 per cent. C. Acid.

800 c.c. British gum paste.
200 „ 50 per cent. China clay.
50 grms. citric acid.

Sighten with Indigo extract. Both these acids are used as resists under weak iron mordânts for purples. Other resists may be employed equally well, but the above are simple and effective, and have, moreover, been adopted on account of the good results they yield.

M. Acid (for Reds and Chocolates).

320 litres lime juice 48° Tw.
320 ,, neutral citrate L.J.
72 kilos. dark British gum.
40 ,, light ,, ,,
40 ,, starch.
$7\frac{1}{2}$ litres turpentine.

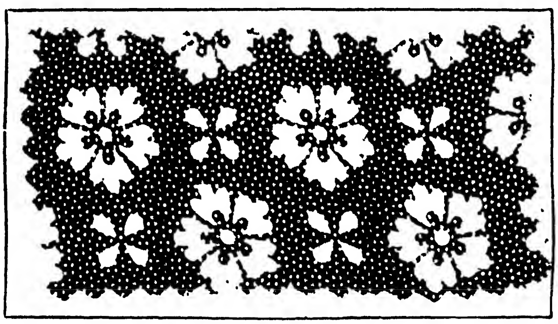
Boil and cool.

Neutral Citrate L.J. = (lime juice 48° Tw. neutralised with caustic soda 70° Tw.).

Resist C. (Reds and Chocolates).

35 litres tartrate of chromium 40° Tw.
10 ,, water.
25 kilos. dark British gum.
10 ,, citric acid.
5 ,, oxalic acid.
$12\frac{1}{2}$,, British gum paste.

Boil and cool.



Resist under Madder Chocolate cover (I.C.I.).

M.S. Resist (Reds, Chocolates).

160 litres lime juice 48° Tw.
16 kilos. starch.
40 ,, water.
48 ,, light British gum.
28 ,, sulphate of soda.

Boil, cool to 50° C., and add—

8 kilos. sulphuric acid 168° Tw.
20 litres water.

Cool before use.

X. Acid.

60 litres lime juice 48° Tw.
40 ,, caustic soda 70° Tw.
20 kilos. dark British gum.
15 ,, light ,, ,,

Heat to 85° C. and cool.

RESIST S. (Reds, Chocolates, and Purples).

6 litres 50 per cent. gum Senegal solution.
2·75 kilos. citric acid.
1 kilo. bisulphate of soda 52° Tw.
0·25 ,, turpentine.

Add a little acid scarlet to sighten.

R.B. RESIST (to resist alumina mordants and Aniline black).

20 litres water.
6 kilos. citric acid.

Add carefully—

10 kilos. soda ash,

and then thicken with—

$\left\{\begin{array}{l}1\frac{1}{4}\text{ kilos. glycerin.}\\ 8\ \ ,,\ \text{light British gum.}\end{array}\right.$

Resist Red (Chocolate and Purple mordants).

Resist red consists of the ordinary 6 T. or 8 T. Reds, plus an extra quantity of tin crystals. The percentage of tin crystals may be indicated thus: 8 T. Red 5 per cent. T. The amount of tin crystals varies with the strength of the iron mordant to be resisted, but it rarely exceeds 75 grms. per litre of colour, although for fine patterns, and for resisting heavy iron mordants, as much as 100 grms. per litre (1 lb. per gal.) is sometimes used. Stannous chloride (tin crystals) acts as a resist or a reserve by reason of its reducing powers: during the ageing process the oxidation of the iron on those parts of the cloth to which resist red has been applied is prevented, while the fixation of alumina which is independent of actual oxidation takes place as usual, so that on dyeing in Alizarin, a red on a purple or chocolate ground is obtained. Any depth of red can be dyed by varying the concentration of the red liquor employed.

The successful production of bright, full resist reds depends quite as much upon the composition of the red liquor as upon its percentage of available alumina. Two red liquors which yield practically identical results in ordinary Madder work are often found to give widely different results when used for *resists* under iron mordants, although under other conditions they both deposit the same amount of alumina on the fibre in the ageing and dunging operations. This matter was investigated, on a practical scale, by the late Mr J. W. Jones of Middleton, and formed the subject of a paper by him entitled "On the Composition and Testing of Tin Red Liquors" (*Textile Colourist*, vol. i. p. 189, 1876). As the result of a long series of trials, he found that when a red liquor of 16° Tw. contained an amount of undecomposed sulphate of alumina corresponding to *more* than 2¾ per cent. SO_4 it was unsuitable for resist Madder reds. The unsuitability took the form of poor, thin, dull colours; hence, since most commercial red liquors are sulphate-acetates of alumina, it is essential, in order to secure the best results, to ascertain beforehand whether they contain too much free sulphate for resist reds. If so, they can easily be rectified by the addition of either a little normal acetate, or by precipitating the sulphuric acid with a calculated quantity of acetate of lime or acetate of lead.

RESIST 12 T. RED 7½ per cent. T. (for strong Chocolate pads and covers).

100 litres red liquor 12° Tw.
20 kilos. flour.
2½ litres oil (olive).

Boil, cool, and add—

7½ kilos. tin crystals.

For purple covers and pads 1½–7½ per cent. of stannous chloride is used according to the strength of the purple mordant.

Resist or Reserve yellows consist of nitrate of lead and varying percentages of citric or tartaric acids. They are treated as already described for Madder yellows. As a rule, resist yellows are thickened with flour in preference to starch or British gum, a little oil being added in the boiling to soften the paste and improve its working properties.

5. T. Resist Yellow (for dark purple covers and pads).

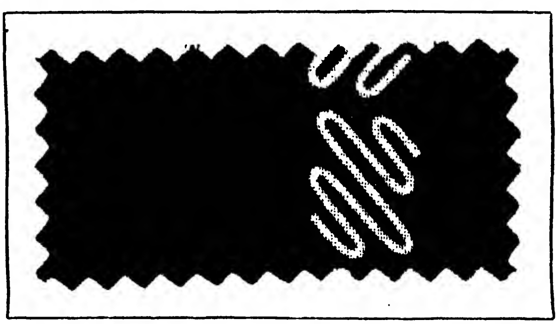
100 litres water.
30 kilos. lead nitrate.
10 „ flour.
1¼ litres olive oil.

Boil and add—

5 kilos. powdered tartaric acid.
2½ „ Indigo extract for sightening.

For weaker purple mordants the tartaric acid is reduced. Cover patterns in general require a rather weaker resist than pads printed in the same mordant. The following strengths of acids, resists, or reserves are arranged to be printed on goods afterwards padded with two rollers at once—the one a pin and the other a line pad.

5 per cent. T. acid	under	20 P. Purple (on M. prep., see p. 464).
3 per cent. „	„	100 „ „
2 per cent. „	„	240 „ „
Resist C.	„	8 Chocolate, 8 P. Purple „
Resist S.	„	12 Chocolate, 8 T. Red, 6 P. Purple.
M.S. Resist	„	12 T. Red.
„	„	12 T. Black (M. prep.).
M.S. Resist ½	„	6 T. Red.
„	„	8 T. Red.
M.S. Resist 1¼	„	4 Chocolate 1½.
M. acid	„	12 T. Red, 8 Chocolate, 12 Choc., etc.
„	„	10 T. Black (M. prep.).
R.B. Resist	„	Aniline Black Cover and 6 or 8 T. Red Pad.
Resist 12 T. Red 7½ per cent. T.	„	8 Chocolate, M. prep.
„ „ „ 5 „	„	20 P. Purple.
5 T. Resist Yellow	„	„
2 T. Resist Yellow	„	240 P. Purple, etc.



White Resist under Madder Purple cover (C.P.A.).

Another Yellow resist under strong Red and Chocolate mordants is made as follows:—

STRONG RESIST YELLOW.

80 litres water.
20 „ citrate of soda 32° Tw.
10 kilos. China clay.
10 „ flour.
30 „ lead nitrate.
1¼ „ olive oil.

Boil, cool, and add—

20 „ citric acid (powdered).
3 „ Indigo extract (sightening only).

If any of the foregoing reserves run or swell in the process it is advisable to grind them up with about 10 per cent. China clay, or, better still, the clay may be introduced during the preparation.

In resist styles that are both covered and padded, the covering and padding are usually done in two separate printings; but an arrangement by W. W. Wilson and the Calico Printers' Association is in use for the continuous printing of the two on an ordinary machine. The cloth, after passing under the covering roller, runs into a drying chamber, situated under the printing machine, from whence it re-enters the machine and is at once printed by the padding roller. In this way considerable economy is effected in time and labour, the cloth being printed twice only instead of the three times necessitated by the usual process.

Another modification of the ordinary printing machine, patented by T. Hindle [1] in 1921, goes still further in the direction of economical working, inasmuch as it not only allows of a two- or three-colour pattern being printed, covered, and padded at a single operation, but also disposes effectually of the main practical objection to this mode of working, viz. the great (and costly) inconvenience of providing covering and padding rollers of the same circumference as the rollers of the pattern over which they are to be printed. This facility of using together rollers of two different sizes is obtained by the simple expedient of slipping a free, or loose, cog-wheel on the axle of the printing bowl or cylinder, an axle which is lengthened for the purpose, and protrudes through the side of the machine opposite to that on which the crown-wheel (the main drive) is situated. The covering or padding rollers are geared with the crown-wheel and drive the cylinder in the customary manner; the pattern rollers, on the contrary, are geared with the freely revolving cog-wheel, and are *driven by the cylinder*, with which, of course, they are in frictional contact. The object of the loose cog-wheel is to keep the rollers of a two- or three-colour pattern "in fit"; if they were not geared with it, through box-wheels, it would be impossible to keep the pattern properly adjusted because the rollers, being dragged round by friction, would be certain to get out of register almost as soon as printing commenced. As it is, any gaining of one roller over another (due to minute differences in size) is checked by the teeth on the box-wheels and loose cog-wheel respectively, since they are in mesh with each other and cannot jump a tooth. Generally speaking, only two sizes of rollers are printed together, but in certain instances it is possible to add a third, which, as it obviously cannot be geared with either the crown-wheel or the loose cog-wheel, must be simply a covering or padding roller, not required to register in any particular way with the other rollers, and driven by friction with the cylinder—a method common in practice for certain styles of work when an odd roller forms part of the final effect.

[1] English patent No. 172403, T. Hindle, 1921.
American „ „ 1416712, „ „
French „ „ 527895, „ „

Apart from the ordinary *cover and pad* styles, the improvement outlined above lends itself to many modifications of superposed patterns, such, for instance, as printing a two- or three-colour check design over a large conventional design in several colours; and for the many effects of superposition produced for the African market. On the commercial side it is of equal importance in that it increases the speed of production and decreases correspondingly the cost of labour and steam—three most important factors in the cost of production.

Colours for cover patterns are almost invariably thickened with flour and starch in order to ensure a sharp impression and a strong colour; padding colours, on the contrary, are as often as not thickened with British gum or a mixture of British gum and flour, and they are, as a rule, worked much thinner than ordinary printing colours, the object, of course, being to secure a good level ground colour by allowing the mordant to soak into the cloth.

The fact that any cover pattern can be printed over any other pattern (in resist colours) makes it possible to obtain an endless variety of combinations of patterns, and, within the limits of the colours suited to the process, of colour also.

The following concrete examples of some of the effects producible by covering and padding cloth previously printed with acids or resists will give some idea of the possibilities of the process.

(1) White Design on a Chocolate ground spotted with Red.—First print M.S. resist or M. acid on M. prepared cloth; then dry and cover in resist 8 T. Red 7½ per cent. T. with a spot pattern; dry again, and finally pad in 8 Chocolate; dry.

(2) White on a Purple and Red ground.—Print M.S. resist; dry and cover in resist 12 T. Red 5 per cent. T.; dry and pad 20 P. Purple.

(3) White, Purple, and Black on Purple ground.—Print 3 per cent. T. acid, 12 P. Purple, and 10 T. Black or Sulphide Aniline Black, on M. prepared cloth. Dry and pad 100 P. Purple or 60 Gum Purple.

(4) White, Yellow, and Red on Dark Chocolate ground.—M. prepared cloth. Print M.S. resist, Strong Resist Yellow, and Resist 8 T. Red 7½ T. Dry and pad 8 Chocolate or 4 Chocolate ½.

(5) White, Yellow, Purple, and Black on Purple ground.—M. prepared cloth. Print 2 per cent. T. acid, 2 T. Resist Yellow, 8 P. Purple, and 10 T. Black. Dry and pad 200 P. Purple or 120 Gum Purple.

(6) White, Red, Yellow, Purple, Brown, and Black on a Purple and White Ground.—On M. prepared cloth. Print first 5 per cent. T. acid, Resist 14 T. Red 5 per cent. T., 5 T. resist Yellow, 16 P. Purple, Catechu Madder Brown, and 10 T. Black. Then dry and cover 20 P. Purple.

(7) White and Aniline Black under Aniline Black cover and Madder Red pad.—First print R.B. resist and Aniline black; then dry and cover Aniline black (prussiate); dry and pass twice through the rapid ager; pad 6 T. Red.

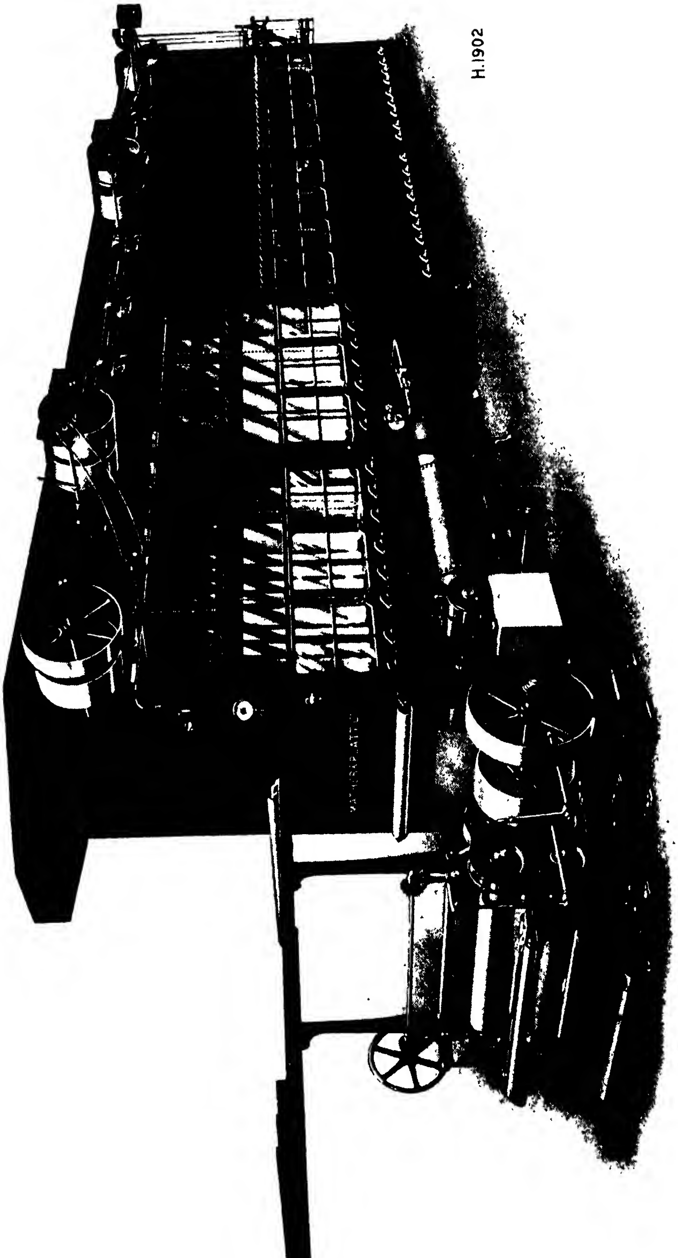
(8) Myrtle and White on figured Green ground.—Print first 6 T. Black and Resist C.; then dry and over print 8 or 12 P. Purple; age, dung, and dye in—

Resorcin Green (for 100 kilos. cloth).

3 kilos. dinitroso-resorcin 50 per cent. paste.
6 ,, glue solution 25 per cent.
2000 litres water.

Raise gradually to the boil and boil ¾–1 hour; wash well and clear by a run through the clearing machine.

After the *final* printing the resist styles, 1-7 above, are aged, and then dunged



Padding Machine with Hot Flue.

[*To face p.* 479.

and dyed, etc., as usual, according to methods already described. Patterns containing resist yellows are treated in exactly the same way as Madder yellows, but if they have no white in them the clearing operations in weak bleaching powder may be omitted.

A style of resist work in which both sides of the cloth are alike, is produced by printing first of all one of the foregoing acids, and then, after drying well, padding the goods "straight through the nip" in a padding mangle; that is, passing the cloth between the indiarubber and brass bowls of the mangle without allowing it to pass through the liquor contained in the box below them. The lower or brass bowl revolves partly immersed in the padding liquor, and carries sufficient of it up to saturate the cloth thoroughly (see fig. 56). From the mangle the cloth runs immediately over a set of drying cylinders, and is dried as rapidly as possible to avoid any chance of the printed resists spreading beyond their proper limits. Resists for this style of work are best thickened with flour or starch, both of which are more insoluble than the gums. China clay may also be added with advantage. In other respects the treatment of these goods is as above, viz. like all Madder dyed goods.

Discharging of Slop-padded Mordants.

This modification of the Madder style is exactly the reverse of that just described. The cloth is first mordanted uniformly all over by padding through solutions of iron or aluminium acetate, and thoroughly dried in hot air; the patterns are then printed upon it in strongly acid discharging mixtures, which act in precisely the same manner as the preceding resists and acids. After printing, the cloth is aged, dunged, and dyed in much the same way as the ordinary Madder styles, but the acid, being printed on partly fixed mordants, must be allowed sufficient time to react with them, or its action must be intensified by a short steaming in the rapid ager, followed by a 24 hours' hanging in a warm, moist atmosphere. The latter procedure is most commonly adopted at the present time.

The original method of drying in hot air was to pass the padded goods through a long brick chamber—the hot flue—which was heated by the hot air rising from the surface of an exposed iron or fire-brick flue (or series of flues) running from end to end of it. The flue itself was heated from a furnace placed at one end of the apparatus. In modern hot flues the heating of the air is effected by means of steam chests and batteries of gilled steam pipes combined with a fan which blows hot air through the whole chamber. The padding mangle is directly connected with the hot flue, so that the mordanted goods pass directly from the mangle into the drying chamber.

A hot flue of the latest type is illustrated on Plate XIV. It is adapted to the preparation of cloth for all styles of printing which involve slop-padding processes and demand thorough but not drastic drying. The chamber is constructed of steel framing and sheet-iron panels, and ample provision is made for access to and inspection of the interior by means of hinged doors and windows on each side. The bearings of the copper rollers, over which the cloth runs, are machined so that when mounted on the framing they are in perfect alignment and consequently the cloth runs smoothly throughout the length of the machine without creases or curled selvedges. A number of the larger top rollers are driven by mitre wheels and cone pulleys from the cross-shaft of the padding machine which is situated in front of the chamber, and means are provided for adjusting the tension on the cloth throughout the apparatus. The temperature may be regulated to suit various classes of work. In the first two sections of the chamber the drying is effected by a combination

of steam chests and hot air. The chests are each arranged between two laps of cloth and the hot air is obtained from the main supply furnished by a fan through a multitubular heater situated beneath the first two chambers. In the last two sections the drying is completed by hot air alone, the air being discharged into them from the heater and distributed by means of sheet-iron trunks arranged along each side, from which trunks it is discharged through vents and slotted pipes placed between the laps of the cloth. The vapours given off by the drying cloth are removed from the chamber by an exhaust fan and are conveyed outside the building through appropriate trunking. The padding mangle attached to the machine has two brass or vulcanite bowls and one of indiarubber, the latter idling or floating between the other two, which are positively driven. The guide rollers in the padding-box are arranged so as to allow of the cloth receiving two immersions with a squeeze after each, thus assuring a thorough saturation. The machine is capable of a large output and, as the cloth never comes into direct contact with heated surfaces, it is particularly suitable for the padding of mordants, naphthols, Indigosol colours and Aniline blacks, and all other colours, etc., which are injured, or prematurely developed, by excessive drying on steam-heated cylinders.

The process of producing white patterns on coloured grounds by the discharging of slop-padded mordants, followed by dyeing in Madder and other colouring matters, was formerly distinguished from all other kinds of dyed work by the name of the Foulard or Padding Style—a name which at one time indicated that the colours were dyed on iron or alumina mordants. The definition of the Padding Style has now been extended, however, to include all classes of work, in which either the mordants or the colours are, of necessity, applied by slop-padding in a mangle, so that the discharging of padded Red and Chocolate mordants is no longer *the* padding style, but only *a* padding style—one amongst many.

Reverting to the application of alumina and iron mordants, it may be noted that the padding style is almost exclusively confined to the production of dark, full colours; and this because, as is well known to practical men, it is somewhat difficult to mordant cloth evenly in the padding mangle with very dilute mordants, which are liable to dissociate irregularly in the hot flue. This defect has, to a great extent, been remedied in the modern hot flues, which are heated by steam and a forced draught of hot air; but alongside these improved means of drying, equal advance has been made in the art of dyeing; and although it is now possible to slop-pad very weak Madder red, Chocolate, and Purple mordants with considerable certainty of success, other methods than Madder dyeing have been devised for the production of discharge effects on light grounds.

After padding and drying, the mordanted cloth is printed with other mordants for colours or black, and with one of the following acid discharges for white:—

DISCHARGE WHITE I.

$\begin{cases} 4 \text{ kilos. starch.} \\ 2\frac{1}{2} \text{ litres water.} \end{cases}$
$6\frac{1}{4}$,, gum tragacanth thickening $1\frac{1}{2}$ per cent.
15 ,, lime juice 48° Tw.

Boil and add—

4 kilos. bisulphate of soda.

Cool and add—

$\frac{3}{4}$ kilo. oxalic acid.

DISCHARGE WHITE II.

300 grms. citric acid.
10 ,, oxalic acid.
690 ,, British gum paste.

DISCHARGE WHITE III.

40 kilos. citric acid.
1¼ ,, oxalic acid.
100 litres water.
5 kilos. China clay.
25 ,, British gum.

The printed cloth is aged through the rapid ager or by hanging for 2 to 4 days with or without a previous run through the ager, and is then dunged twice, first at the *boil* for 3 minutes in the continuous fly dunging machine, and second for half an hour as usual at 60° C. After dunging it may be dyed with any suitable dyestuff. The fly dunging at the boil enables the acids to *cut* the mordants much more effectually than they would at a lower temperature.

(1) BLACK AND WHITE ON RED GROUND:—(1) Pad the cloth in red liquor at 8° Tw.; dry. (2) Print on 6 T. Black and Discharge White I.; dry. (3) Age, dung, and dye in Alizarin as for reds. (4) Oil, steam, soap, and clear.

(2) WHITE ON BROWN OR CINNAMON GROUND.—(1) Pad the cloth in 40 Chocolate liquor (40 parts Red liquor 8° Tw., and 1 part Iron liquor 24° Tw.); dry. (2) Print on Discharge White III.; dry. (3) Age, dung, and dye in the following:—

1½	per cent.	Alizarin, yellow shade, 20 per cent.	On the weight of the cloth.
15	,,	Bark extract 48° Tw.	
10	,,	Persian berry extract 48° Tw.	
½	,,	chalk.	
20	,,	glue solution 15 per cent.	

(4) Wash well, bran for ¾ hour, steam, and clear.

(3) WHITE ON BLACK GROUND.—(1) Pad in the following:—

3 parts Iron liquor 24° Tw.
5 ,, Red liquor 14° Tw.
2 ,, water.

Dry. (2) Print on Discharge White II. (3) Age, dung, and dye in—

10	per cent.	Logwood ext. 40° Tw.	On the weight of the cloth.
1	,,	Sumach ext. 48° Tw.	
1	,,	chalk.	
20	,,	glue size 15 per cent.	
½	,,	soda-ash.	
½	,,	Turkey-red oil.	

(4) Wash well, bran at 80° C. for half an hour, wash, dry, and clear in bleaching powder solution ⅛° Tw. A light soaping enhances the brilliancy of the white after chemicking.

(4) WHITE ON CLARET GROUND.—Proceed as in (1), omitting the black, but dye up in Alizarin bordeaux.

(5) YELLOW ON RED GROUND.—Proceed as in (1), omitting the black, and after dyeing and clearing the red, pad in a weak solution of a basic acetate of lead; dry partially, and pass through ammonia vapour to fix the lead as hydrate, and then develop Chrome yellow by a run through bichromate of soda, 5 grms. per litre. Wash well and dry.

Scores of other colours can be dyed on slop-padded and discharged red and black liquors, but the above will serve to illustrate the methods of work without giving further examples.

Combined styles with Madder dyed colours and Indigo have never been produced in very large quantities, on account of the practical difficulties that crop up between the ageing and the dunging of the printed mordants. Many attempts have been made to combine the Madder style with the glucose process of Indigo printing, and some good work has been done in this way, but on the whole the process is difficult to work successfully on the large scale. The Indigo loses in depth of shade during the drastic clearing operations that are essential to the production of a bright red and a pure white ; and again, after the reduced Indigo has been re-oxidised in cool hanging rooms, it ought to be washed well in cold water, whereas the mordants printed along with it require dunging in hot solutions. In any case one or the other must suffer to some extent, and consequently the style is but little used.

Aniline black in combination with alumina and iron mordants constitutes one of the most important of all styles of printing. The process of ageing is common to both, and the dunging operations not only fix the mordants but at the same time improve the black ; and if a Prussiate black is employed, the iron it contains acts as a mordant, thereby tending to tone the shade of the black, while increasing its depth.

Goods printed in Madder red and chocolate mordants and sulphide or vanadium Aniline blacks are usually aged by hanging in the ageing chambers for 3 to 4 days (if this system is available) ; if printed with the prussiate Aniline black, the black is developed by one or two runs through the rapid ager, followed at once by a passage through gaseous ammonia to neutralise the free mineral acid liberated by the steaming. In other respects the treatment of the goods is identical with that given in the description of the previous processes for ordinary printed mordants such as 6 T. Red, 20 Chocolate, etc.

(*b*) **The Basic Style.**—Of late years the employment of basic Aniline colours in the dyed styles has increased considerably. They yield a vast variety of beautiful shades, moderately fast to light and soap ; and as they can be dyed on any insoluble tannate, it is possible to apply them to the production of effects analogous to those obtained by Madder dyeing in most of its aspects. For this purpose it suffices merely to treat goods mordanted with red or iron liquor in a boiling solution of some tannin matter, and then, after a good washing, dye them in a slightly acid solution of a basic colour. Both iron and alumina form insoluble tannates, and these fix basic colours practically as well as tannate of antimony. From this it is evident that any iron or alumina mordant, whether printed directly, or resisted, or discharged, can be utilised for obtaining a range of effects altogether too wide to enumerate in detail. In this way (by tanning iron and alumina mordants) most of the Madder styles can be reproduced in a series of bright colours otherwise unobtainable by any dyeing process in vogue before the discovery of coal-tar dyestuffs.

Another method of applying basic colours by dyeing is to print tannic acid on the cloth, then fix in tartar emetic, wash well, and dye. By printing several strengths of tannic acid, various shades of the same colour are obtained by a single operation in the dye beck ; and the tone of these same shades can be varied either by fixing the tannic acid with copperas ($FeSO_4$) instead of with tartar emetic, or by treating the tannate of antimony mordanted cloth in a solution of copperas before dyeing. In both instances the bluish-grey tannate of iron is formed, and this modifies the tone of the colour subsequently dyed.

Still another, and perhaps the most important method of applying basic colours in dyed styles of calico printing, is that based upon the observation that

tannic acid and tannate of antimony mordants are capable of being discharged by caustic soda under the influence of steam. The cloth is first mordanted all over by padding, and is then printed with a thickened solution of caustic soda, steamed, washed, and dyed in a basic colour. The caustic soda dissolves out the mordant from the printed parts, and in the dye bath these parts remain undyed, so that they form white figures on a coloured ground. For working details of the Tannin Discharge Style, see Discharge Styles.

BASIC COLOURS ON ALUMINA AND IRON MORDANTS.—Patterns produced in this way are printed as usual with red or chocolate mordants, and for black, with Aniline black. After ageing and dunging they are tanned in tannic acid or one of its many substitutes, *soaped lightly*, well washed, and dyed. The soaping is not absolutely essential, but it facilitates, in a marked degree, the production of a pure white and a good full quality of colour.

BLACK AND WHITE ON VARIOUS GROUNDS.

Process :—

(*a*) Print Aniline black (prussiate) and 4 T. Red.
(*b*) Age twice through the rapid ager, and after gassing in ammonia vapour allow to lie 2 days in loose bundles.
(*c*) Dung, wash, and tan in—for 100 lbs. cloth (full pattern)—

2 per cent. tannic acid	}	Dye half an hour at 70° C., wash well in warm water.
$\frac{1}{16}$ „ ammonia		

(*d*) Soap at 50° C. for 10 minutes in 1 part soap per 1000 of water. This process is optional. Wash well until free from soap.
(*e*) Dye as follows for medium shades :—

$\frac{1}{2}$–$2\frac{1}{2}$ per cent. dyestuff.
2 „ acetic acid 6° Tw.
$1\frac{1}{2}$ „ alum.
water (a sufficiency).

Raise the temperature of the dye bath to 80° C. in half an hour, and then dye a further $\frac{1}{2}$ hour at that temperature. Wash well.

(*f*) Soap at 60°–70° C. until the whites are clean, and then finish with a thorough wash.

Examples :—

Rose pink	$\frac{1}{2}$ per cent.	Rhodamine B.
Blue	$\frac{1}{4}$ per cent.–$\frac{1}{2}$ per cent.	Methylene blue N.
Electric	$\frac{1}{2}$ per cent.	New blue L (Cassella).
Green	$\frac{1}{2}$ „	Methylene green (yellow shade).
	$\frac{1}{2}$ „	Auramine O.
Orange	$1\frac{1}{2}$ „	Auramine O.
	$\frac{1}{4}$ „	Rhodamine 6 G.
Violet	$\frac{1}{4}$ „	Methyl violet.

Darker shades are obtained by operating on exactly the same lines, but with a stronger alumina mordant to start with, followed by a corresponding increase in the quantities of tannin and dyestuff.

Thus :—

	Print.	*Tan.*	*Dye.*
Navy blue . .	6 T. Red	3% tannic acid	3% New fast blue R.S.
Crimson . .	„	„	$1\frac{1}{2}$% Methyl violet 6 R.
Plum . . .	8 T. Red	4% „	$1\frac{1}{2}$% New fast blue R.S.
			$1\frac{1}{4}$% Methyl violet 6 R.

	Print.	*Tan.*	*Dye.*
Peacock green, dark	6 T. Red	3% tannic acid	3% Methylene green (yellow shade).
Olive . . .	,,	,,	2% New fast blue R.S. 1½% Auramine O.
Myrtle . . .	8 T. Red	4% ,,	2% Indigo blue J. A. (Geigy). 3% Thioflavine T.
Dark blue . .	8 Choc.	3% ,,	2% Marine blue S.

Any of the above colours dyed on a Chocolate mordant give duller shades, the dullness depending on the proportion of iron present. Two- and three-colour effects are obtained by printing different strengths of mordant, say, 14 T. red, 4 T. red, and ½ T. red. Tan and dye as above.

Basic Colours on Printed Tannin Mordants.—In this method a thickened solution of tannic acid is printed on white cloth, and then fixed by a run through tartar emetic or other suitable antimony salt. If quieter shades are required, the fixing in antimony may be followed by a short treatment in a weak solution of ferrous sulphate. This style is not much used, although it yields good *cameo* effects in a single dyeing.

Two-Colour effect on White Ground.

Process :—

(*a*) Print on white cloth the two following thickened solutions of tannic acid :—

5% Tannin Mordant.
- 500 grms. tannic acid.
- 2 litres acetic acid 9° Tw.
- 5½ ,, gum tragacanth 6%.
- 2½ ,, water.
- 10 litres

¾% Tannin Mordant.
- 1½ litres 5% tannin mordant.
- ½ ,, acetic acid 9° Tw.
- 4½ ,, tragacanth 6%.
- 3½ ,, water.
- 10 litres

(*b*) Dry after printing, and age twice through the rapid ager. Ageing is not essential unless the pattern contains Aniline black, but it is advantageous, as it seems to fix the tannic acid on the fibre better. Fix in the ordinary tartar emetic bath—

15–20 kilos. tartar emetic,
5 ,, chalk,
1000 litres water,

and wash well.

(*c*) Dye in any basic colour which does not stain the white parts of the pattern permanently.

For Pink	say	1 per cent.	Rhodamine 6 G.
,, Blue	,,	2 ,,	Thionine blue O.
,, Yellow	,,	2 ,,	Acridine yellow G.
,, Green	,,	1½ ,, ½ ,,	Acidine yellow G. Thionine blue O.
,, Navy blue		2–3 ,,	New fast blue R.S.

and various mixtures of Pink, Blue, and Yellow, for browns, olives, and other mode shades.

Slop-padding of Basic Colours.—The dyeing of mixtures of basic colours in the dye beck or on the jigger presents many difficulties in practice, especially if the shades dyed are delicate and light in tone. Some dyestuffs

combine with the mordant very quickly, even in the cold, while others dye up more slowly, the result being that, in most cases, the ultimate colour is more or less uneven in shade. Greater regularity can be secured by the addition of acetic acid to the dye bath, but this cannot be carried beyond a certain limit, and even then it is not a perfect levelling agent, although with care good results are obtained. The best method of dyeing level shades with small percentages of mixed basic dyestuffs is to *slop-pad* the mordanted goods through an acid solution of the colours, instead of dyeing them in a larger bulk of water, as is necessarily the case in the dye beck, and to a less degree in the jigger. After padding, the goods are dried over steam-heated cylinders or through a hot flue, and then passed, in the rope state, into a dye beck filled with boiling water—the scalding-off beck. During this process of scalding off, which lasts 15–30 minutes, the dyestuff is completely fixed on the fibre, and the colour that washes out of the unmordanted parts of the cloth is so completely taken up by the mordanted parts that the water in the dye beck is scarcely stained. Indeed, the fixation of the colour is so far advanced after padding and drying that cold water hardly affects the mordanted parts of the cloth at all, dissolving out only that portion of the colour which adheres to the whites or unprinted parts.

In order to obtain regular results the pressure of the squeezer bowls of the padding mangle ought to be regulated in such a way that the cloth carries its own weight of dye liquor into the drying apparatus ; and a three-bowl mangle ought to be used in preference to a two-bowl machine, because it is possible to arrange it so as to allow of the cloth passing twice through the padding liquor, with a squeeze between each passage—an advantage which ensures a better penetration of the dyestuff into the body of the fabric.

Examples of padding liquors :—

LIGHT OLIVE (100 kilos. cloth).

1 per cent. dyestuff =	30	grms.	Rhodamine 6 G.
	725	,,	Acridine yellow G.
	245	,,	Thionine blue O.
	10	litres	acetic acid 9° Tw.
	90	,,	water.

FAWN (100 kilos. cloth).

1 per cent. dyestuff =	80	grms.	Rhodamine 6 G.
	900	,,	Acridine yellow G.
	20	,,	Thionine blue O.
	10	litres	acetic acid 9° Tw.
	90	,,	water.

Slop-pad any tannin-mordanted cloth in the above dye liquors, at a speed and with a pressure on the mangle bowls that will allow the cloth to absorb its own weight of liquor. Then dry ; scald off for 20 minutes at the boil ; wash and soap as required.

The two chief advantages of the slop-padding method of dyeing basic aniline colours are—(1) great uniformity of shade ; and (2) increased output, due to the speed at which the goods are dyed. A saving of dyestuff is also effected, because practically none comes off in the hot-water becks, while in ordinary dyeing the bath is rarely exhausted. Purer colours, too, are obtained, and any modifications of shade that may be necessary are rapidly and easily made. To see the shade yielded by any mixture, all that is required is to dip a part of the cloth under treatment into the dye liquor, pass it at once through

the mangle by hand, dry it sharply, and wash it immediately in about 25 times its own weight of boiling water; then dry it again, and compare it with the standard to be matched.

The disadvantages of working as above are—(1) that the cloth requires drying before padding; and (2) that the drying apparatus must be cleaned for each colour dyed. If, however, the first few dry cans are wrapped with calico, this second objection is of little moment. Most of the soiling takes place on the first four or five cans, and if these be wrapped it is a simple matter to change the wrapping. Of course, if pinks follow greens, the whole range will require cleaning by running wet grey cloths for some time, taking care to see that their position on the cans is altered continually so as to make sure that the whole working surface of the drying cylinders (cans) is clean. But, as a rule, pinks and similar delicate colours are padded on mangles specially reserved for what are known as clean colours, the dirty colours—greens, blues, slates, purples, etc.—being padded on other machines.

The slop-padding method is only economical for large quantities of goods. The extra drying operation is then more than counterbalanced by the improved quality of the work as regards uniformity and evenness of shade in the different lots, and increased speed of production, owing to the fact that hundreds of pieces can be dyed continuously. For small orders the ordinary methods of dyeing are the cheapest and most convenient; and even if they are somewhat liable to give irregular results, and demand more care in their working, they at least do away with the necessities of previously drying the cloth and of cleaning down the drying machines at frequent intervals.

(*c*) **The Chrome Mordant Dyed Style.**—Chromium mordants, except when mixed with colouring matters as in the steam style, are rarely printed as such, owing to the practical difficulties in fixing them satisfactorily when so applied. The ordinary chromium acetates, sulphate-acetates, and nitrate-acetates all deposit a certain amount of chromium oxide on the fibre, but it is unevenly distributed, and as a rule gives irregular work when dyed up.

It might be supposed that chromium acetates would behave like the acetates of iron and aluminium, but this is not the case by any means. Such chromium compounds as are capable of application by printing are too stable to dissociate during the ageing process, *with one exception*, and in practice they do not seem even to decompose fully—certainly not regularly—on steaming. On the other hand, those compounds that readily yield their chromium to the fibre are only suitable for padding in a slop-padding mangle, because, although they dissociate easily enough, they do so too rapidly and unevenly during their run through the drying apparatus of the printing machine. Moreover, in presence of thickening agents, they are exceedingly liable to decompose spontaneously, with disastrous results if the printing is proceeded with before the decomposition of the mordant is observed. On the whole, therefore, chromium mordants may be regarded as unsuitable for printing, except in combination with colouring matters as in the steam style.

The above-mentioned exception to the general rule is not, properly speaking, a chromium compound, but a mixture of bichromate of potash, magnesium acetate, sodium thiosulphate, and a little ammonia. This mixture, thickened with starch paste or British gum, is stable in the cold, or at the ordinary temperature and without access of light, but when printed, dried, and steamed the constituents react upon each other. Under the influence of steam and magnesium acetate, the thiosulphate reduces the bichromate to the basic state, and chromic oxide is deposited on the fibre. The printed goods are then either washed at once, or they may be passed quickly through a 5 per cent. solution of soda-ash at the boil, in order to ensure the complete precipitation of the

chromic oxide. Any colour that is used with chromium mordants in the steam style is suitable for dyeing on chromium mordanted cloth obtained as above.

The dyeing is carried out as already described for Madder colours, the only difference being that the goods require no oiling or steaming, though these processes do in some cases improve the brilliancy of both colours and white. As a rule, however, a good soaping, followed by a light chemicking, is quite sufficient to clear the whites.

Either a steam Logwood black or a prussiate Aniline black may be printed in combination with this mordant; both resist the dyeing operation, but Aniline black must be used if it is intended to fix the mordant in soda-ash after steaming. A recipe for the preparation of a steam chrome mordant will be found in the section on Mordants.

Basic acetates and basic sulphates of chrome, thickened with tragacanth, are sometimes used for printing on goods mordanted with chromium oxide (by any of the usual padding processes). They are fixed by a short steaming and a run through boiling soda-ash. On dyeing, a two-tone effect is obtained; or if black and a discharge acid have been printed along with strong chrome mordants, on cloth lightly mordanted all over with any of the mordants suitable for that purpose, a four-colour effect is produced, consisting of a black, white, and dark chrome colour, on a lighter ground of the latter. Used in this way, basic acetates and sulphates of chrome are useful mordants, but used alone, on white cloth, their irregularities are too pronounced for them to be of much use in practice except for multicolour dyed work, in which their unevenness is, to some extent, masked by the other shades.

A reduction mordant similar to, and suggested by, the above steam chrome mordant of Koechlin was worked out by one of the authors in 1904. It was never introduced on the large scale, although it gave satisfactory and consistently good results in a series of bulk trials. The original experiments were made with the old hydrosulphite N.F., but any similar sulphoxylate will answer quite as well. Of the two recipes given below, the second is perhaps the better; strict comparison, however, was not made.

	I.	II.
Bichromate of soda	3,000 grms.	3,000 grms.
Caustic soda 88° Tw.	2,000 ,,	..
Water	10,000 ,,	9,600 ,,
Sodium acetate	..	2,750 ,,
Ammonia 25 per cent.	..	500 ,,
Sulphoxylate-formaldehyde	1,500 ,,	1,500 ,,
Gum tragacanth 6 per cent.	33,500 ,,	32,650 ,,
	50,000	50,000

Print on white cloth, dry, age twice through a hydrosulphite ager at 100°–102° C.; pass for 2 minutes through a boiling 2 per cent. solution of soda-ash; wash well and dye in Alizarin, Cœruleïn, Alizarin heliotrope B.B., Alizarin orange, Anthracene brown, Gallocyanine, Persian berries, or Quercitron bark, or any other mordant colour which gives a pleasing shade on chrome mordants.

By replacing the greater part of the tragacanth with water, the same mixture may be used for slop-padding with excellent results, as judged by the limited number of experiments made.

Taken altogether, the printing-on of chromium mordants is of comparatively little importance. Similar effects and a greater variety of them can be obtained more easily, rapidly, and with greater certainty of success from the same colours by *direct printing*, as in the steam style.

The discharging of *padded* chrome mordants, and of padded steam chrome colours, is one of the more important branches of modern calico printing. The previously mordanted cloth is printed with citric acid, and then aged, fixed, and dyed. The acid dissolves out the mordant, with the result that a white pattern on a coloured ground is obtained. Similar styles are produced by printing oxidation discharges on cloth padded with ordinary steam colours. The padded goods are dried, printed at once with the discharge, and steamed as usual. Details of these processes will be given in the section dealing with Discharge and Resist Styles.

Remarks on the Dyed Style in general.

In all dyed styles in which part of the cloth is left unmordanted, or in which very light colours are employed, it is essential to the attainment of successful results, as represented by bright level colours and pure whites, that the following precautions be observed :—

(1) The cloth must be thoroughly bleached. To test this, dye a fent off the pieces in question in Alizarin before the cloth is put into work : no streaks, cloudy patches, or stains of any sort ought to be apparent, and the slight tint given by the Alizarin ought to come out on soaping.

(2) Cloth that has been used for back greys ought not to be employed for the dyed styles. It is often very difficult to bleach out the last traces of the colour and mordants that have been transferred to back greys from the printed cloth ; and if they are allowed to remain, they invariably dye up, showing as a faint secondary pattern. Such back greys may appear perfectly white after bleaching, and are quite suitable for the steam styles or Aniline black discharge styles, but for the Madder styles it is best to avoid all risk by employing new greys only. These should be bleached until they are perfectly free from all foreign matters whatsoever, otherwise they are practically certain to contract stains in dyeing.

(3) The mordants must be properly fixed by the ageing and dunging processes, and before the goods are entered into the dye bath they must be freed from all traces of the thickening agents used in printing. Neglect of these points means uneven colours or stained whites.

(4) In order to secure pure whites, the dyed goods must be thoroughly washed in water to remove all loosely adhering dyestuff before they are submitted to the oiling and steaming processes.

(5) The dyeing must be conducted at a temperature not exceeding 75° C. for Alizarin and other mordant dyestuffs, unless the cloth be prepared in oil, when it may, with advantage, be dyed at a higher temperature.

(6) The final operations of soaping must be sufficiently drastic to clear the whites and brighten the colour, by removing that portion of the latter which lies, more or less, on the surface only. Too much reliance ought not to be placed on the bleaching properties of the bleaching solution used in the last operation of all. If this has to be repeated two or three times to brighten up a dirty white, the colour is certain to suffer both in brightness and depth.

(7) In dyeing basic colours, keep the dye bath on the acid side by the addition of acetic, formic, or sulphuric acid or potash alum. These assist greatly in preserving the purity of the white.

Other dyed styles based upon one or other of the foregoing are in use, but they are either modifications or combinations of those already given, and call for no special mention.

Patterns produced by the discharging of Turkey red, Indigo, etc., may be regarded, in a sense, as belonging to the Dyed Styles. Their characteristic

features, however, are due entirely to the application of discharging agents, and therefore, although the preliminary dyeing of the cloth is certainly an essential (and the first) stage in their production, they must be classed as *discharges*; and as such they will be described, along with other Discharge Styles, in another part of this work. The dyeing of the cloth, however, may be conveniently dealt with here.

Turkey Red.

Turkey red is merely a Madder or Alizarin red, dyed by a special and lengthy process which renders it not only excessively bright, but also extremely fast to all the various destructive agencies to which textile fabrics are exposed.

Turkey red may be considered as quite fast to light, soap, weak mineral acids in the cold, weak alkalies, and to all but the most powerful oxidising and reducing agents. In short, it is one of the fastest colours known.

The dyeing of Turkey red is a specialised branch of the industry practised only by a few large firms. It involves a long series of consecutive operations, for the proper performance of which an extensive installation of special plant is required; hence it can never form part of the routine work of the smaller printworks, whose output all told would be too small to cover cost of production. Turkey red of a sort is dyed in many works, but it compares very unfavourably with the magnificent productions of the great firms who make it a speciality.

The distinguishing feature of Turkey red is the preparation of the cloth in olive oil, or its preparations, the "Turkey-red oils" of commerce. Castor oil oleines and other sulphonated oils are also used with success.

The employment of pure hot olive oil, with its accompanying processes of drying at a high temperature and passing through soda baths, has become almost, if not altogether, obsolete since the introduction of "soluble oils." Formerly it was necessary to pad the cloth 4–8 times through olive oil emulsions, followed by long exposures to the air, and a 2 hours' drying in stoves at 60° C. after each padding. The oiling, therefore, took several days to accomplish, not to speak of the time subsequently occupied in passing through soda-ash solutions, steeping in water to get rid of the soda, treating in sumach, mordanting, dyeing, and clearing. The whole process was a question of weeks.

The greatest improvement in Turkey-red dyeing, and one which shortened the process to days, was made by Steiner of Accrington, who impregnated the cloth with the necessary amount of oil in a single operation. This was effected by padding the cloth through *hot* olive oil, kept at a constant temperature of 110° C. The oxidation of the oil was commenced by hanging the goods for 2 hours in a stove (hanging chamber) maintained at 70° C. The goods were then taken out and passed, in the open width, 6–7 times through a solution of soda-ash 4° Tw., followed by a stoving of 2 hours at 75° C. after *each* passage. They were finally treated at 40° C. in a ½° Tw. solution of soda-ash, dried 2 hours at 70° C. after washing out the soda, and then mordanted, dyed, and cleared in much the same way as in modern processes.

Steiner's process, in turn, gave way to the present-day methods, which yield equally good reds, and, when properly carried out, equally fast ones. For discharge work, it is not necessary to dye a shade quite as fast as is required for plain reds, for in any case the red ground will long outlast the colours printed upon it; and if it is fast enough to withstand a run through a powerful decolorising agent like bleaching powder at 16°–18° Tw., it leaves little to be desired on the score of fastness.

Those interested in the old processes will find detailed accounts of their practical working in *A Manual of Dyeing*, by Knecht, Rawson, and Loewenthal, or in *The Dyeing of Textile Fabrics*, by the late J. J. Hummel.

In most modern processes the frequent and tedious operations of passing the cloth through alternate baths of olive oil emulsions and solutions of sodium carbonate, followed by stoving after each, have been replaced by a *single* run through soluble Turkey-red oils, followed by one stoving or one steaming process. This is especially the case for Turkey reds that are intended for discharging. For the fastest reds, however, the oiling and stoving are often repeated four or five times, and the treatment in dilute alkaline solutions is also practised, with questionable reason ; probably it is a survival of the older methods, though it is not unlikely that a final run through soda-ash removes superfluous oil from the cloth, and renders it more capable of attracting the mordant.

The Turkey-red oil (oleine, sulphonated oil, soluble oil, etc.) used may be prepared from either olive or castor oil. As already described, these are treated with sulphuric acid, and the resulting sulphonated compounds are neutralised with caustic soda, ammonia, or a mixture of the two. These neutralised oils are the Turkey-red oils of commerce.

The steaming or stoving of the cloth after oiling is not absolutely essential to the production of a bright, full red, but the oil must be decomposed at some stage of the process, and therefore, if the cloth has been mordanted in aluminium salts before steaming, the necessary decomposition of the oleine is brought about by dyeing at the boil. Oiled cloth, whether steamed or not, possesses the property of attracting and fixing the mordant ; and, according to Liechti and Suida, on *unsteamed* cloth the mordant consists of the aluminium compounds of both the ethers and the fatty acids, while on *steamed* cloth it consists of normal aluminium oxyoleate or trioxyoleate, according as olive or castor oil has been employed.

The addition of tin to the aluminium-oil mordant improves the shade of the red. The tin may be introduced as stannate of soda into the oil prepare, or as stannous chloride into the acetate, or the basic sulphate, of alumina mordant.

Lime is another essential constituent of the Turkey-red lake ; and if the water used for dyeing is not calcareous, an addition of chalk or acetate of lime must be made to the dye bath. It can also be introduced by fixing the aluminium mordant in a warm dunging bath containing chalk—a process which is usually adopted, if only to ensure the complete fixation of the mordant.

In the dyeing operation the temperature is better kept at about 70° C., especially if the cloth is only lightly charged with oil ; if, however, a larger amount of oil is present in the fibres, the temperature may be raised, at the end of the dyeing, to the boil, though no useful purpose is served thereby, unless it happen that the oil-prepared cloth has been mordanted in alumina without a previous stoving or steaming, in which case the oil mordants undergo the necessary decomposition at the higher temperature.

On emerging from the dye bath the goods are of a dull reddish-brown shade, totally unlike the brilliant red into which they are converted by subsequent processes. This brown colour is a compound of aluminium alizarate and basic aluminium oxyoleate or trioxyoleate, together with a small quantity of calcium oxyoleate. When its basicity is neutralised by means of a second oiling and steaming it becomes a bright red, the brilliancy of which is further increased by subjecting the goods to a long boil in soap and a small quantity of stannous chloride, followed by a quick run through acid, and a final run through hypochlorite of soda.

The following is a résumé of a process used on the large scale for the pro-

duction of a bluish Turkey red dyed specially for discharging: the cloth used is only half-bleached, experience having shown that the finest reds are obtained on goods that have not been treated in bleaching-powder solutions. Half-bleaching consists in boiling the grey cloth twice in caustic soda, followed by souring and washing after each boil. The first boil lasts for 10 hours at 8–15 lbs. pressure in any type of kier; the second boil occupies 6 hours at from 4–15 lbs. pressure. The goods are not dried after bleaching, but simply squeezed to free them from excess of water; they are then sent directly through the processes given below.

Turkey Red for Discharging.

(1) Slop-pad the cloth direct from the bleach-house, before drying, through a 1 per cent. solution of olive oil oleine, and dry over copper cylinders.

(2) Prepare (slop-pad) in 5 per cent. olive oil oleine; stove 2 hours at 70°–75° C.; pass through a solution of carbonate of soda at 1½° Tw.; wash through one beck in the open width, and dry. The soda and wash becks are worked in sequence, and the drying machine is also arranged to work with them, so that the process is continuous.

(3) Prepare again in 5 per cent. oleine, dry, and steam in loose bundle form for 1½ hours at 4 lbs. pressure (cottage steamer).

(4) Prepare the cloth after steaming in—

7½	kilos.	stannate of soda.
30	litres	ricinoleate of ammonia 50 per cent.
1000	,,	water.

This solution is contained in a machine similar to a fly dunging range, and provided with a pair of mangle bowls at the exit end. The cloth runs through at the rate of 30 yards per minute, and is in the liquor about 3 minutes; dry and stove 2 hours at 60° C., or simply dry and allow to lie in pile until wanted.

(5) Mordant, in a similar machine, through basic sulphate of alumina 8° Tw. or red liquor 8° Tw., both at a temperature of 35° C. Dry over copper cylinders.

(6) Repeat (5), and allow to lie a day or two.

BASIC SULPHATE OF ALUMINA.

$\left\{\begin{array}{l}\text{300 kilos. alum.}\\ \text{3000 litres water.}\end{array}\right.$

Add gradually—

$\left\{\begin{array}{l}\text{41¼ kilos. soda-ash.}\\ \text{1000 litres water.}\end{array}\right.$

(7) When the goods are wanted for dyeing, fix them in a solution of binarsenate of soda and chalk at 40°–50° C. The fixing is performed in a continuous machine of at least 4 becks, provided with top and bottom rollers, over which the cloth travels in the open width.

1ST BECK.

5000	litres	water.
100	,,	binarsenate of soda 18° Tw.
50	,,	glue size 15 per cent.
2½	kilos.	chalk.

2ND BECK.

5000	litres	water.
5	,,	binarsenate of soda 18° Tw.

3RD and 4TH BECKS.—Warm water.

After fixing as above, wash again, and proceed without drying to—

(8) DYEING.

6	per cent.	Alizarin 20 per cent.	blue shade.
5	,,	,, ,,	yellow shade.
$1\frac{1}{2}$	,,	ground sumach.	
$2\frac{1}{2}$	,,	Turkey-red oil 20 per cent.	

Raise the temperature of the dye bath gradually during the course of an hour to 75°–80° C., and continue dyeing at that temperature for half an hour. Take out of dye, wash well, squeeze, and without drying—

(9) Prepare in 5 per cent. olive oil oleine, partly neutralised with ammonia. Dry, and then—

(10) Steam for 1 hour at 5 lbs. pressure. Wash and clear.

(11) *First Clearing.*—Boil the goods for 3 hours at 4 lbs. pressure with 4 per cent. soap (palm oil, cotton-seed oil, or Marseilles), 3 per cent. soda crystals, 0·2 per cent. stannous chloride, 2 per cent. oleine (40 per cent.), and a sufficiency of water. Wash well in spiral washing machines, and proceed to the second clearing without drying the goods.

(12) *Second Clearing.*—Boil again for 3 hours at 3-4 lbs. pressure with 2 per cent. soap, 3 per cent. castor oil soap (50 per cent.), 0·2 per cent. stannous chloride, and sufficient ammonia to dissolve the stannous ricinoleate precipitated; take out, wash thoroughly to remove all traces of soap, and, without drying, proceed to the final brightening processes.

The boilers in which these clearing operations are carried out are of different types: some are practically identical with and work with the same intermittent action as the ordinary low-pressure bleaching kier—that is, the clearing liquor is circulated through the goods by means of a puffer pipe and a steam jet or a steam injector; others are simply large jacketed or double-cased pans, like a colour pan, but stronger, and fitted with lids which can be bolted down to make a steam-tight joint with the rim of the pan. Steam may be admitted to the interior of the pan, and the lid carries a safety valve. The liquor, therefore, can be boiled both by live steam and by the steam circulating between the inner and outer casings of the pan. Whatever type of clearing boiler is adopted, it must be made of copper, since it is obvious that, at high temperatures, the goods would be stained by coming into contact with iron. In many works the clearing boilers serve the double purpose of clearing and steaming the dyed goods. For the second steaming (operation 10) the oiled and dried goods are packed loosely in the boiler, and then steamed as long as required at the necessary pressure.

(13) *Brightening.*—After the second clearing the now bright red cloth is further treated in order to give it the well-known brilliancy of a true Turkey red. For this purpose it is passed in the rope form through successive baths of—(1) hydrochloric acid $1\frac{1}{2}$°–2° Tw.; (2) cold water; (3) and (4) warm water; (5) soap; (6) and (7) hot water; (8) cold water; (9) soda chemick 3°–4° Tw.; and (10) water. All these operations are performed in a continuous machine, furnished with squeezing bowls at convenient intervals, to prevent the successive baths becoming too highly contaminated with the liquor carried forward by the cloth from the preceding becks.

(14) Finally, the cloth is washed thoroughly, hydro-extracted, and dried by hanging in stoves, at a low temperature.

A faster and more intense Turkey red is obtained by padding the cloth 4 times in a 5 per cent. solution of ammonia-soda olive oil oleine, followed each time by a 24 hours' stoving at 70°–75° C. A light treatment in dilute soda-ash

(1° Tw.) is then given, and, after drying, the cloth is mordanted, dyed, cleared, and brightened as above.

Another method of dyeing Turkey red was worked out and patented by Erban & Specht. In this process the Alizarin is dissolved in ammonia and then diluted with lime-free water, and mixed with the requisite quantity of Turkey-red oil. The cloth is padded in this solution, dried in the hot flue, and then passed at once through a second bath containing the necessary mordants. The development and fixation of the colour lake are brought about by steaming the goods for 2 hours, commencing without pressure, and finishing at a pressure of 2 atm. After well washing, the red is treated as already described.

Turkey Red (Erban-Specht Process).

(1) Pad the bleached goods in—

20 kilos. Alizarin paste 20 per cent.
5 litres ammonia 25 per cent.
40 ,, ammonia-soda oleine 25 per cent.
lime-free water to 100 litres.

(2) Dry in the hot flue, allow to cool, and then pass cold through the following mordant:—

2 litres red liquor 8° Tw.
½ ,, acetate of lime 28° Tw.
7½ ,, water.

Dry in the hot flue and then—

(3) Steam for 2 hours as follows:—

1 hour without pressure.
½ ,, at a pressure of 1 atmosphere.
½ ,, ,, ,, 2 atmospheres.

(4) Wash well, and soap with 2 per cent. soap at the boil for 15 minutes.

(5, 6, 7, 8, etc.) Clearing and brightening operations as for other Turkey reds.

It may be noted in passing that Erban & Specht's process is applicable to other mordant colours, and also to iron and chromium mordants. It is not much used for Turkey-red dyeing in this country, if at all.

Goods intended for discharging by the acid process may be dyed with any brand of Alizarin; free chlorine destroys both blue and yellow shades of red. On the other hand, the *caustic soda* discharging process is best suited for the yellow shades, the blue shades yielding good whites only with difficulty. Indeed, red and pink effects are frequently produced by taking advantage of the greater resistance of bluish reds to caustic soda. The cloth is dyed with a mixture of blue and red shade Alizarins, and is then discharged with caustic soda just sufficiently strong to dissolve out the yellow Alizarin- or Flavopurpurin-lake.

Indigo Dyeing (*for Printing Purposes*).

The method of dyeing Indigo on vegetable fibres is based upon its property of being converted by reducing agents into indigo-white, which is readily soluble in alkaline solutions. When cotton is impregnated with these solutions and then exposed to the air in the wet state, the indigo-white is re-oxidised to insoluble indigotine, and as this is precipitated in the fibres themselves the resulting colour is fast. The alkaline solution of indigo-white constitutes the **Indigo vat.**

The reducing agents used in practice are ferrous sulphate or copperas, zinc powder, zinc foil, and hydrosulphite of soda, and the alkaline solvents are for the most part confined to lime and caustic soda. The ingredients composing the vat give it its distinguishing name.

The Ferrous Sulphate or Copperas Vat is rarely ever employed nowadays for dyeing Indigo-blue intended for calico-printing purposes. The white given by discharging is not so pure as that obtained on a blue dyed in a zinc or in a hydrosulphite vat, besides which a large amount of sediment is always present in the copperas vat, and as this contains a good deal of Indigo, it entails considerable loss unless steps are taken to recover the Indigo. In any case a certain quantity of dyestuff is always lying useless at the bottom of the vat in the form of a bulky flocculent precipitate of a compound of ferrous oxide and indigotine. In view of the fact that the copperas vat has been replaced by more suitable methods, it is not considered necessary to go further into the details of its manipulation.

The Zinc-Lime Vat.—Zinc powder in presence of Indigo and lime rapidly reduces indigotine to indigo-white. Thus—

$$C_{16}H_{10}N_2O_2 + Ca(OH)_2 + Zn = C_{16}H_{12}N_2O_2 + ZnO_2Ca$$

The indigo-white dissolves in the excess of lime present, and the solution forms the dye vat.

The proportions of the ingredients employed in setting the zinc-lime vat vary according to their quality, and, when natural Indigo is used, according to the percentage of indigotine that it contains. Taking the synthetic products, Indigo L.L., or Indigo S.C.I.B., as pure indigotine, the following proportions will represent approximately the relative amounts used on the large scale.

STOCK INDIGO-WHITE.

20 kilos. Indigo (or 100 kilos. 20 per cent. paste).
40 „ slaked lime.
80 litres water at 45° C.

Mix well together and add—

12 kilos. zinc powder.

Stir well, and maintain at a temperature of 40°–45° C. for 6-8 hours, stirring up well from time to time. While the reduction of the indigotine is proceeding the rest of the vat may be set as follows:—

4000 litres water.
1 kilo. zinc powder.
4 kilos. slaked lime.

Stir well to deoxidise the water, and then add as much of the stock solution of indigo-white as is required. Rake up frequently, and then allow the precipitate to settle. If the vat is in good working order, it ought to be sufficiently clear to use in about an hour or an hour and a half after the stock solution has been added.

If desired, the same vat may be made by mixing all the ingredients together in the first instance with about 12 kilogrammes of coarse iron filings and borings, which act mechanically, and promote the more rapid reduction.

A good zinc-lime vat has a substantial blue scum or "flurry" on its surface, is of a clear amber colour, and when stirred up shows broad blue veins all over its surface.

Another zinc powder vat is made by replacing lime with caustic soda thus:—

$$C_{16}H_{10}N_2O_2 + Zn + 2NaOH = C_{16}H_{12}N_2O_2 + ZnNa_2O_2$$

The indigo-white dissolves in the excess of caustic soda present in the vat. Zinc hydrate is soluble in excess of alkali, with which it combines to form zincate of soda ($ZnNa_2O_2$), as shown in the above equation; and as an excess of caustic soda is essential to dissolve the reduced Indigo, it follows that a portion of the zinc is always in solution. The alkalinity of the vat must not be pushed too far, however, otherwise both the shade of blue and the cloth itself are liable to suffer.

Both the zinc-lime and the zinc-soda vats are liable to the defects of muddiness and frothing, due to the slight but continuous evolution of hydrogen. If these defects are slight, it is usually sufficient to stir up the vat for a short time and then allow it to settle again before use; but if they persist after this treatment, an addition of Indigo must be made, since the evolution of free hydrogen (giving rise to froth, and keeping the sediment in constant motion) only takes place in presence of excess of zinc, and after the Indigo has been fully reduced. In these circumstances, the longer the vat is allowed to stand the worse it becomes, and nothing will improve it but the addition of further Indigo, followed by a vigorous raking up. After standing for 1½ hours the vat should then be settled sufficiently to allow of the dyeing operations being resumed.

Although the initial cost of zinc powder vats is greater than that of copperas vats, they offer counterbalancing advantages which render their use more economical. In the first place they are very simple to set, and then, again, the absence of ferrous hydrate reduces the loss of available Indigo by at least half—that is, from about 20 per cent. to 10 per cent.; and even this loss is not due to the formation of an insoluble compound of Indigo, but to the fact that a good deal of the reduced Indigo remains as such in the useless sediment at the bottom of the vat.[1] As the vat is exhausted, this Indigo can be brought into use again by stirring it up with more water and a little alkali, in which case it serves as a weaker vat for light shades. Little by little, therefore, the sediment can be washed almost free from indigo-white; or, conversely, the amount of indigo-white it absorbs can be kept almost constant by reducing the quantity of stock solution added to replenish the vat. Another great advantage of the zinc-lime vat is that the precipitate it contains is, at most, only about one-sixth of that in a copperas vat of the same strength. Moreover, this precipitate is much denser, and consequently settles more rapidly, so that the vat is ready for dyeing in a shorter time, especially if iron borings be added. In the case of the zinc-soda vat, the precipitate is still further reduced, but the vat is rather more difficult to manage. On the whole, the zinc-lime vat is very easy to work. It yields even shades; and as it contains comparatively little sediment, it can be used for a much longer time than the copperas vat, which requires cleaning out five or six times as often. Any Indigo remaining in the sediments can be recovered by boiling the latter with a cheap reducing agent, filtering off, or settling what zinc or lime is undissolved, and then oxidising the solution of indigo-white by exposing it to the air in shallow tanks, or by pumping it through spray pipes or a perforated trough arranged at some height above the containing tank, into which it is allowed to fall again through the air. In this way, by constant circulation, the indigo-white is thoroughly aerated and oxidised, and the precipitated indigotine only requires to be washed and filtered to a paste of known percentage to be again available for use.

The zinc-lime and the zinc-soda vats are chiefly employed for dyeing calico in continuous machines, but the former is also eminently adapted for

[1] A part of the loss has been shown to be due to the formation of isatin in the vat (Crowther, *Jour. Soc. Dyers and Colourists*, p. 146, 1911).

"dipping vats," and is largely used both in England and on the Continent for the production of the Indigo Resist or Reserve style.

The Hydrosulphite Vat.—The reducing agent employed in this vat is hydrosulphite of soda, a salt which is prepared in practice by acting on bisulphite of soda with metallic zinc. (See Reducing Agents.)

In presence of caustic soda or milk of lime, this salt reduces indigotine to indigo-white, which dissolves in the excess of alkali present, forming a vat—

$$C_{16}H_{10}N_2O_2 + Na_2S_2O_4 + 2NaOH = C_{16}H_{12}N_2O_2 + 2Na_2SO_3$$

On the large scale, caustic soda is generally replaced by *milk of lime*. Lime vats are said to dye more evenly than those made up with caustic soda, and to keep in good working condition longer, owing to the fact that a thin film of calcium carbonate forms over the entire surface of the liquor and protects it from the oxidising action of the air. At the same time, caustic soda is employed largely in some works, and with excellent results.

The presence or absence of sediment in hydrosulphite vats depends upon the method adopted for setting them. If a sediment is not objectionable, it is cheaper and quicker to make a strong stock solution of indigo-white, by mixing together, in a cask, all the ingredients of the vat, in proper sequence, and then, when the Indigo is fully reduced, to add the whole mixture to the requisite quantity of water in the dye vat or beck. The vat is then allowed to settle in the usual way before it is used for dyeing.

When the dye vessels are too shallow to permit of working in this manner, or when, for any other reason, it is desired to have a perfectly clear vat, the alkaline hydrosulphite must be prepared separately, and filtered from zinc hydrate, etc., before it is added to the Indigo. This occupies some time, and entails the use of a special but cheap apparatus for the manufacture of the alkaline hydrosulphite. If, however, a high yield of a concentrated solution of the salt is required, a filter press will be necessary to extract as much liquor as possible from the useless precipitate thrown down by the alkali used for neutralising the acid salt.

Hydrosulphite vats are set in three different ways:—

(1) With zinc powder, bisulphite of soda, lime or caustic soda, and Indigo.

(2) With specially prepared sodium hydrosulphite, Indigo, and caustic soda or milk of lime.

(3) With commercial solid hydrosulphite of soda, Indigo, and caustic soda or lime.

The two latter methods are practically identical, save that in the one the reducing agent is prepared by the dyer himself, while in the other it is bought ready-made. As prepared in the dye-house, the hydrosulphite, if not used at once, must be stored in well-corked carboys, and kept in a dark, cool place, otherwise it rapidly oxidises; but even if air be excluded it deteriorates.

The Zinc-Bisulphite-Soda Vat.—This hydrosulphite vat is largely used in practice; it contains some sediment, but otherwise is as suitable for most kinds of Indigo dyeing as the clearer vats.

(*a*) Stock Solution.

25 kilos. bisulphite of soda 76° Tw.
25 ,, water.

Add gradually, whilst stirring—

5 kilos. zinc powder.

Stir ½ hour, allow to stand ½–¾ hour, and then add—

25 litres caustic soda 77° Tw.
50 kilos. Indigo 20 per cent. paste,

Stir well, and then add water at 45° C. to bring the whole up to 200 litres. Stir again for ¼ hour, and set aside in a warm place until the solution becomes a golden yellow; the Indigo is then completely reduced, and ready for adding to the vat.

(*b*) THE DYE VAT.

A vat holding about 2500 litres is partly filled with water (say 1700 litres) at a temperature of 40° C.; the following solution is then added to it to deprive it of its free oxygen before the stock solution of reduced Indigo is put in:—

500	grms.	bisulphite of soda 76° Tw.
1500	,,	water.
75	,,	zinc powder.

Mix well, allow to react for ½ hour, and then pour into—
1700 litres water at 40° C.
¼ litre caustic soda 77° Tw.

Stir up well, and add—
200 litres above stock solution of Indigo.

Make the whole to 2000-2250 litres with water, rake up well, and allow to settle, when the vat is ready for dyeing. The vat thus made contains about 5 grms. of Indigo per litre, and is suitable for dyeing dark shades.

Lime (in the proportion of 650 grms. of slaked lime to every litre of caustic soda) may be used in place of caustic soda in the preparation of the foregoing vat. It gives more sediment, however, but in other respects it is quite as good as the above soda vat.

The Clear Hydrosulphite Vat.—In preparing this vat, which is merely a modification of the preceding, the reducing agent is freed from zinc salts before it is allowed to act on the Indigo. This is effected in the following way:—

Mix 50 litres of bisulphite of soda 76° Tw. with 80 litres of water at not above 30° C., and then add gradually 7½ kilos. of zinc powder beaten up with 7½ litres of cold water. Stir until the mixture becomes nearly white, then allow to settle. Decant the clear liquor, and add to it 7½ to 8 litres of caustic soda 76° Tw., or a corresponding quantity of milk of lime. Allow to settle again; filter off the precipitate after decanting the clear liquor, pass it through a filter press, and add the filtrate to the rest of the solution. Finally, set at 36° Tw. and use at once.

The vat is made up as follows:—

(*a*) STOCK SOLUTION 5 per cent.

25	kilos.	Indigo 20 per cent. paste.
30	,,	milk of lime (20 per cent. quicklime).
20	,,	hydrosulphite of soda 36° Tw. as above.
25–30	,,	water.
100 litres		

Heat to 55° C., at which temperature the Indigo is completely and rapidly reduced, forming a clear yellow solution. If the solution is of a decided green colour the reduction is incomplete, and more hydrosulphite of soda must be

added; and if, on the other hand, a dense white precipitate settles out, it indicates a deficiency of lime. The precipitate is undissolved indigo-white, and disappears on the addition of lime or caustic soda.

(*b*) THE DYE VAT ½ per cent.

$\left\{\begin{array}{l}\text{1790 litres water at 45° C.}\\ \text{10 ,, hydrosulphite of soda 36° Tw.}\end{array}\right.$

Stir ¼ hour and then add—

200 litres stock solution of Indigo 5 per cent.

2000 litres

The dye liquor should always contain a slight excess of hydrosulphite, otherwise it oxidises quickly, and becomes both green and turbid. It contains no sediment, and consequently the dyeing can be proceeded with immediately the vat is set.

The continuous running of cloth through the liquor has the effect of churning it up; and if, from this or any other cause, the vat becomes green owing to excessive oxidation, the dyeing must be stopped at once, and a little fresh hydrosulphite added to the vat. In this way the Indigo is reduced again and the vat is immediately available for further work. Excessive alkalinity may be corrected by the careful addition of dilute hydrochloric acid; or if caustic soda is the alkali employed, dilute sulphuric acid will answer the same purpose.

A more convenient method of setting the clear hydrosulphite vat is to employ one of the specially manufactured solid sodium hydrosulphites, but, apart from convenience, these salts offer no other advantage over those prepared by the dyer himself, and as they are expensive, they have not been universally adopted in practice.

For most calico printing purposes the various hydrosulphite vats have proved themselves to be suitable, and especially may that be claimed for the clear vats. The absence of sediment ensures the production of brighter and more regular shades; further, the loss of dyestuff is very small, and, as the vat is comparatively stable, it is always ready for dyeing, and can be used for a long time without cleaning out.

The Dyeing of the Cloth.—The dyeing of piece goods is effected either (1) by immersing them for a certain time in the clear solution of reduced Indigo, followed by draining and exposure to the air, or (2) by passing them through the solution in a continuous manner, and then, after squeezing out the excess of liquor, running them over a system of rollers arranged above the dye vats. This exposure to the air varies with the amount of indigo-white absorbed by the cloth, and must always be sufficiently prolonged to ensure the complete re-oxidation of the indigo-white to indigotine, otherwise the shade will be uneven, owing to the partial removal from the fibre of the unoxidised indigo-white during the subsequent process of washing and souring.

In dyeing by the first or *Dipping Method*, the dried goods are hooked by the selvedges to a rectangular wooden frame furnished with small brass hooks at the top and bottom; each fold is separate, and the cloth is stretched fairly tightly, but not too much so, lest its contraction in the liquor should tear it from the hooks, and not only damage the cloth, but result in uneven dyeing where two folds come in contact. The frame filled with white calico is then lowered into the vat, where it is allowed to remain below the surface of the liquid for 15 or more minutes. At the expiration of this period it is withdrawn and slung above the vat so as to expose the cloth to the air, whereby the reduced

Indigo is re-oxidised into insoluble indigotine. The alternate dips and airings are repeated as often as is necessary to obtain the requisite depth of shade.

A dipping vat is shown in fig. 79.

In the Dipping method it is obviously impossible to dye a level shade with one dip: the liquor drains off the lower selvedge during the exposure to the air, leaving the lower part of the cloth much darker than the upper. Hence,

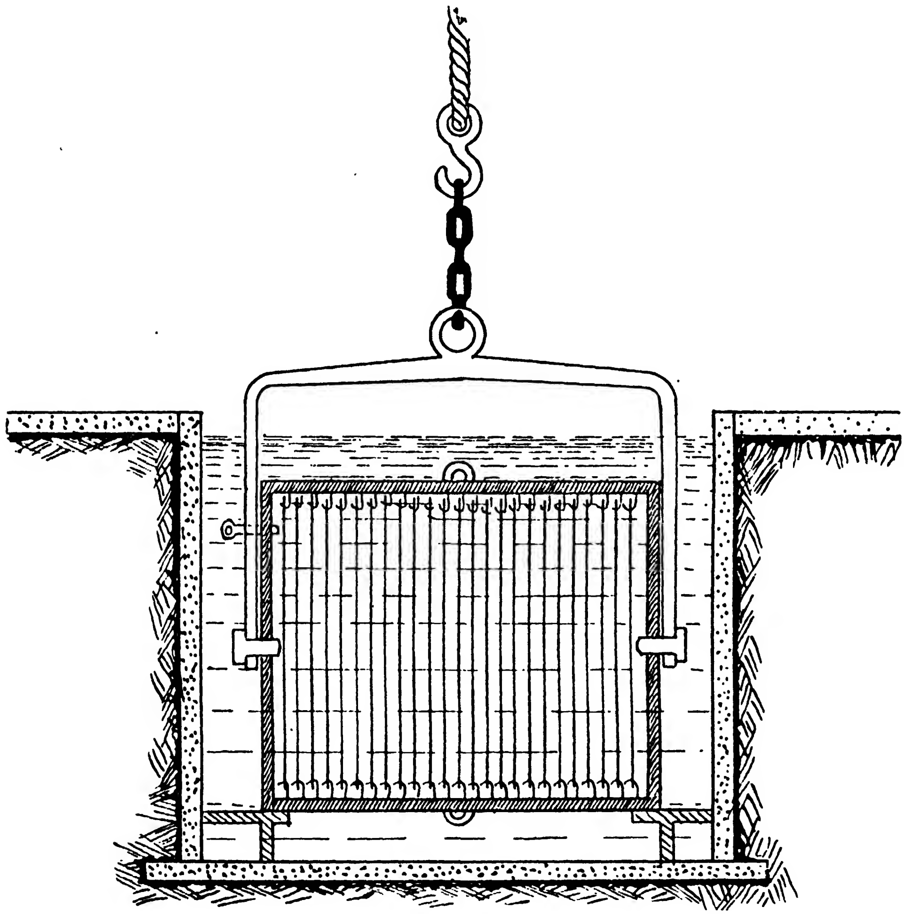


FIG. 79.—Indigo dipping vat.

when the cloth is dipped a second time, the frame upon which it is hooked is reversed, so that what was the top selvedge becomes the bottom one. In this way the liquor drains off from each in turn, and the ultimate shade is quite even. The frame is reversed at every fresh dip.

Other forms of dipping vats are in use, but they are worked on a similar principle, and call for no special mention. The chief use of all dipping vats is in the dyeing of the Indigo Resist Styles, to be described later.

In the second or *Continuous Method* of dyeing Indigo, the goods are passed through the liquor over a system of guide rollers arranged on an iron frame, which fits into the vat in such a way that the rollers are completely immersed.

The frame is removable, so as to allow of the vats being cleaned out or re-set as required. At the exit end of the vat a pair of squeezing bowls is fixed to express the excess of liquor from the cloth as it passes into the air to oxidise before entering a second similar vat. The number of vats through which the cloth passes is regulated by the depth of blue desired, and by the concentration of the dye liquor itself. The continuous Indigo dyeing machine made by Messrs Mather & Platt is shown in fig. 80. From this it will be seen that the cloth passes through several vats in succession, and that between each immersion it is exposed to the air to regenerate the indigotine before it enters the next vat. The airing arrangements are simple, effective, do not pull the cloth, occupy but little space, and are not liable to get out of order. They consist of a wince (C) placed high above the vat and a travelling apron or creeper (D). The cloth, on leaving the vat, is drawn upwards by the wince, which then plaits it down on the creeper. This latter, moving slowly forward, and carrying a long length of cloth, in short loose pleats allows of a large quantity

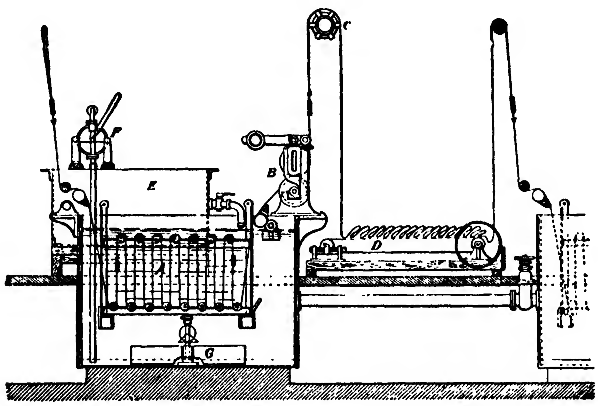


FIG. 80.—Continuous Indigo dyeing machine.

of material being oxidised at once and in a very convenient manner. When the first pleat reaches the end of the creeper, the cloth is again drawn up and down through the air by a roller placed above the second vat, through which it is then drawn by the action of the squeezing bowls at the point of exit. The exposure to air is then repeated exactly as before, and so on for every succeeding vat through which the goods pass, the whole process being continuous. Each vat is also provided with mechanical agitators to facilitate the setting, and with a supply tank at the side for replenishing the vat with fresh indigo-white solution.

When Indigo is dyed continuously as above it is customary to set the vats at different strengths. The first vat may contain anything between $\frac{1}{10}$ per cent. and $\frac{1}{4}$ per cent. of indigotine, while the stronger succeeding vats contain from $\frac{1}{2}$ per cent. to 1 per cent. of indigotine, reckoned on the weight of their liquid content.

Light blues or Sky blues are frequently dyed in a single run, but no attempt to dye a dark blue at a single operation, in a strong vat, ought to be made, since it is practically impossible to obtain a regular shade by this means. The best method is to pass the goods through a series of vats of increasing concentration, and to oxidise them fully between each operation.

After dyeing, the material is allowed to lie a while, then washed lightly, and passed through dilute sulphuric acid (1°–2° Tw.) to remove any alkaline car-

bonates it may contain, and to brighten the shade. When natural Indigo is employed, the tone of blue is improved by a light soaping, which probably removes the greater part of the brown and yellow colouring matters always present in natural Indigo.

The successful dyeing of Indigo is as much a question of practical experience as of theoretical knowledge—perhaps more so. The setting of the vats, their manipulation, and their maintenance in good working condition are comparatively simple matters when once understood; but to understand them properly, and to recognise the characteristic features and the causes of the various defects they are liable to develop during the course of dyeing, requires a long practical acquaintance with dye-house work. The condition of the cloth to be dyed, the speed at which it is passed through the vats, and the quantity dyed at a time, are one and all important factors in the production of satisfactory work. The strength of the vats, too, calls for careful attention, and altogether the whole process of Indigo dyeing demands constant and close observation from start to finish. Further information on the details of Indigo dyeing will be found in the *Manual of Dyeing*, by Knecht, Rawson and Loewenthal.

Indigo Dyeing with Indigosol O.—The properties of Indigosol O. have been discussed already in connection with Indigo printing, and call for no further mention here except in so far as they relate to great simplification in the processes of Indigo dyeing.

Indigosol O., unlike Indigo, does not require any preliminary treatment to convert it into a form suitable for dyeing, nor does it need any special plant to be set apart solely for its application. It is a stable and neutral compound of indigo-white, perfectly soluble in water, and it can be dyed on cotton, silk, or woollen fabrics in any ordinary type of padding-mangle. The ease and uniformity with which even concentrated solutions of Indigosol O. are absorbed by the various fibres make it possible to obtain (by a single short passage through a padding-mangle) a deep level shade of Indigo in one operation only. Such a shade, if dyed with Indigo in any of the ordinary vats described above, would require at least four or five separate dips and airings before its full intensity was developed, and even then great care would have to be exercised to overcome the liability of Indigo to dye unevenly.

Dyeing with Indigosol O. is carried out on similar lines to those employed for printing, viz. (1) by padding the goods in an aqueous solution of the dyestuff, followed, after drying, by oxidation with perchloride of iron; (2) by padding in a solution containing sodium nitrite, from which nitrous acid (the oxidising agent) is liberated during a subsequent passage through sulphuric acid. The first process yields the darker shades; the second is the more convenient, and is generally preferred for resist styles, as the iron salt has a tendency to soil the whites. In both processes the solutions are sufficiently stable for all practical purposes; only after ten or twelve days do they begin to show signs of material deterioration. If still better keeping properties are required, they may be attained by the addition of a small percentage of β-naphthol, which has the remarkable effect of rendering the solutions almost perfectly stable—at least for any reasonable time.

A slight alkalinity of the dye bath (or padding solution) is not undesirable; and, for reserve styles, the addition of glycerine and Turkey-red oil is considered beneficial. For plain dyeings, and dyeings for subsequent discharging, a simple solution is best—especially in the case of discharge styles in which the best results are always obtained on grounds as free as possible from fatty matters.

According to the various purposes to which the dyeing is destined, the following padding solutions are recommended:—

PADDING SOLUTIONS.

	1.	2.	3.	4.	5.	6.
	Grms.	Grms.	Grms.	Grms.	Grms.	Grms.
Indigosol O.	120	120	60	100	60	80
Water at 120° F.	730	730	750	700	750	700
Tragacanth thickening 10 per cent.	15	15	..	..	..	15
Soda ash	4	4	..	..	4	..
Glycerin	..	..	15	20	20	..
Turkey-red oil 40 per cent.	..	..	15	20	20	..
Dissolve at 120° F., cool and add—						
{ Nitrite of soda 98 per cent.	..	30	15	25	15	20
{ Water	..	90	100	100	100	100
{ β-Naphthol	..	..	..	..	..	2
{ Caustic soda 36° Tw.	..	..	..	..	..	3
{ Water	..	..	..	..	..	50
Make up to	1000 c.c.	1000 c.c.	1000 c.c.	1000 c.c.	1000 c.c.	1000 c.c.

Nos. 1 and 2 are used for plain dyed shades; Nos. 3, 4, 5, and 6 may also be used equally well for this purpose, but are more particularly adapted to reserved styles.

The above solutions are padded in a slop-padding mangle, the goods dried, and then oxidised as under:—

No. 1. Pass for one minute at 77/86° F. through a solution of—

30 grms. perchloride of iron 66 per cent.
30 ,, sulphuric acid 96 per cent.
1000 ,, water.

Wash well and dry.

Nos. 2, 3, 4, 5, and 6 are all developed alike by a passage of one minute's duration through—

20 grms. sulphuric acid 96 per cent.,
1000 ,, water, } at 77° F.

followed by a thorough wash, etc.

Lighter shades may be obtained by reducing the strength of the bath.

Padding liquors Nos. 3 and 4 are recommended for reserved styles printed with lakes or pigments fixed with albumen; No. 5 for Basic and vat-colour reserves; and No. 6, which may readily be modified by addition of glycerine or Turkey-red oil, for all purposes to which dyed Indigo is put.

The Indigosol O. process of dyeing Indigo is, as yet, used mainly for specialities, but practical experience of its working has already amply demonstrated that it possesses notable technical advantages over the older methods. It is simple, clean, and reliable in operation; it can be put into use at any time; it allows of dark level shades being obtained by a single short passage through the dye liquor; by its means many long-sought effects may be produced which were impossible with Indigo; and its application demands no special dyeing machinery—in short it is a quick, convenient, and much-improved process. For these reasons it is probable that, other conditions being favourable, the Indigosol O. process will eventually supersede the older and more cumbersome methods of vat dyeing.

(3) THE AZOIC COLOURS.

GENERAL.—Unlike most colouring matters, the *Azoic colours*—or, as they are sometimes called, the *Ice* colours—do not come into the market as dyestuffs ready for application, but are produced on the fibre directly, by the combination of their constituents.

When certain aromatic amines are diazotised and combined with suitable naphthols they give brightly coloured precipitates which are insoluble in water, acids, alkalies, and soap solutions, and are, for the most part, tolerably fast to light. In this state the precipitates are used as pigments, and may be fixed upon cloth, like other pigments, by means of albumen, caseïn, and similar coagulable bodies. But by far the most valuable property of the insoluble Azoic colours is that they can be precipitated on and in the fibre, just as easily as in a liquid medium. For this purpose the cloth is first prepared in an alkaline naphtholate, and, after carefully drying, is either printed with, or passed through, a solution of the requisite diazo compound. The colour is produced almost instantaneously, and is, practically speaking, quite fast; it is very bright in most instances, and being deposited in the body of the material instead of on the surface, as is the case with pigment colours, it resists the usual energetic rubbing processes to which prints are subjected in the domestic laundry. Altogether the Azoic colours, when properly dyed, may be classed among the fastest of colours, many of them equalling the Madder colours in general, Turkey red, Aniline black, and the vat colours.

The term "Azoic" has, of late years, been increasingly applied to the Insoluble Azo colours. It is a better and more descriptive name for them and, as it serves to distinguish them sharply from the vast family of other Azo dyestuffs, it is used in this work.

The beauty and fastness of the Azoic colours, combined with their simplicity of application and their adaptability to a great variety of styles, have gained for them a place of such importance that probably there exists to-day no printworks of any standing in which they are not in use in one form or another.

Although all Azoic colours are formed on the same principle—the coupling of naphthols and phenolic bodies with diazotised amines or diamines—those used in the textile industries fall into two main groups, viz., (1) the colours produced with β-naphthol (and occasionally with α-naphthol), and (2) the colours produced with various substitution products of β-naphthol. These two groups will be described under the separate headings of "The Beta-Naphthol or Older Azoic Colours" and "Naphthol A.S.," respectively.

The Beta-Naphthol or Older Azoic Colours.

Pre-eminent amongst the older Azoic colours are what are known technically as *Para red*, *Naphthylamine bordeaux* and the *Meta- and Ortho-Nitraniline oranges*. Para red is as bright as Turkey red, and Naphthylamine bordeaux or claret and the two oranges are purer and brighter in shade than any clarets or oranges obtained from Alizarin. But none is so fast as the still older competitors, especially to light, and although they have displaced the Alizarin colours to a great extent in many cheap styles, the latter still find considerable employment in better class work—the dyeing of printed mordants, the classic " acid and red, pad pink style," cretonne printing, small garment patterns and other standard styles which are required to possess a high degree of fastness to washing and light.

In addition to red, claret, and orange the β-naphthol colours include various shades of brown, chocolate, puce, blue, and black. A fine pink is also available,

but so far a bright yellow, blue, and green are absent from the range. The different shades and colours are obtained by using different amines in combination with β-naphthol, either alone or with an addition of α-naphthol; and as amines and naphthols respectively can be mixed in any proportions, it is possible to obtain a great variety of effects. It is well to note, however, that in practice such mixtures are never used if, by any chance, they can be avoided; they are unreliable for the most part with β-naphthol combinations and, unless the greatest care and experience are brought to bear on their manipulation, they yield, in bulk work, most unsatisfactory results. Different diazotised amines couple at different rates with β- and α-naphthols, and if mixtures of *both* components are used in the attempt to produce a given shade, the results will not be likely to encourage a second venture. If a mixture must be used, it is better to confine it to one component of the colour—the amino-base or the naphthol—and to allow ample time for the coupling to take place.

Many of the Azoic colours are volatile, and gradually disappear, by sublimation, from the cloth. Those prepared from β-naphthol and its derivatives are not only almost entirely free from this defect, but possess also the further, and inestimable, advantage of being insoluble in caustic soda, whereas those developed on α-naphthol (and phenols) are more or less soluble. Hence, wherever possible, β-naphthol and certain of its compounds are employed; α-naphthol is only used for shading purposes, and then only when other means are not available.

The insolubility in caustic soda of the β-naphthol colours renders them particularly suitable for printing along with strongly alkaline colours like Indigo, other vat dyestuffs, and the sulphur colours; and by working in this way an immense number of fast colour combinations are produced both cheaply and rapidly. The same remarks apply equally to the β-oxynaphthoic acids and their derivatives—Naphthol A.S. and various analogous compounds the application of which will be described at the end of the present section.

The colours obtained by combining the diazo compounds of some of the commoner primary amines with α- and β-naphthols respectively are given in the following table:—

Amine.	α-Naphthol.	β-Naphthol.
* Orthonitraniline	Reddish brown	Orange.
* Paranitraniline	,,	Turkey-red.
Metanitraniline	,,	Bright orange.
Paratoluidine	Warm brown	Yellowish ,,
Orthonitro-paratoluidine	Rich ,,	Orange.
* α-Naphthylamine	Chocolate or Puce	Claret.
β- ,,	,, ,,	Red.
Aminoazobenzene	,,	,,
Ortho-aminoazotoluene	,,	Dull claret.
* Benzidine	Deep chocolate brown	Chocolate.
* Tolidine	,,	,,
* Orthonitro-paraphenetidine	Not used	Fine bluish red.
* Chloranisidine	,,	Scarlet.
* Paranitro-orthotoluidine	,,	Fine orange.
* Dianisidine	,,	Violet.
* ,, with copper	,,	Navy blue.
* Paranitro-orthoanisidine	,,	Bright red.

The amines marked with an * are those chiefly used in practice.

The above colours all stand a short (very short) steaming. This allows of

them being used in combination with certain mordant dyestuffs, Diphenyl black, basic dyestuffs, and pigment colours, as well as with those already mentioned.

The process of producing Azoic colours on the fibre consists of three separate and distinct operations :—

(1) The impregnation of the cloth with naphthol.
(2) The diazotising of the amine or diamine.
(3) The development of the colour.

1. Preparation of the Cloth.

For this purpose the cloth is padded in an alkaline solution of the naphthol to be used ; generally a solution of β-naphthol in caustic soda.

Various other substances are usually added to the naphthol solution in order either to improve the shade of the colour or to preserve the prepared material from becoming brown on drying, or on standing for a day or two. Turkey-red oil, para soap P.N. (ammonium ricinoleate), antimony compounds, and aluminate of soda are all employed to these ends.

According to Lauber and Caberti, the addition of an alkaline solution of antimony oxide prevents the browning of the naphtholated goods during their drying over copper cylinders ; and, furthermore, it preserves them in good condition for dyeing or printing for two or three days if they are stored in a dark, cool place. These statements have been verified in practice, for whereas goods padded in simple naphtholate of soda require to be printed or dyed at once with the diazo solutions, those containing antimony oxide yield satisfactory results after having been kept for two and sometimes three days. The other additions chiefly enhance the beauty of the colour, and besides this, Turkey-red oil keeps the cloth soft and tends to give the colour a more transparent quality.

The drying of naphtholated materials should always be conducted at as low a temperature as possible: α- and β-naphthols are volatile, and if dried too hard they sublime, leaving the cloth unevenly impregnated, with the obvious result that in dyeing the colour develops irregularly.

For plain dyed shades it is usually unnecessary to make any of the above additions, though, of course, they exercise no detrimental influence on the shades obtained. But plain shades are dyed chiefly for discharge printing, and it is an axiom in this style of work that the freer the cloth is of unnecessary bodies, the cleaner, sharper, and brighter are the patterns discharged upon it ; so that, apart from the extra expense, the presence of oil, soap, etc., is apt to be injurious.

β-Naphthol itself gives a yellow shade of red with Paranitraniline, which is not suitable for all markets. To correct this it is mixed with a small quantity of Shading salt R., or is replaced altogether by Naphthol R., which is really a mixture of ordinary β-naphthol with the shading salt (the sodium salt of β-naphtholmonosulphonic acid F.). Still bluer shades of red and pink are obtained from nitrophenetidine and β-naphthol. Particulars of naphthol solutions will be found further on.

2. Diazotising.

Primary amines, when treated under suitable conditions with nitrous acid, are converted into diazo compounds, the distinguishing feature of which is that the chlorides contain the group Ar—N : N—Cl. Diazobenzene chloride

is the simplest, and will serve as a type of all the various bodies. It is obtained from aniline thus—

$$\underset{\text{Aniline hydrochloride.}}{C_6H_5NH_2.HCl} + \underset{\text{Nitrous acid.}}{HNO_2} = \underset{\text{Diazobenzene chloride.}}{C_6H_5N:N.Cl} + 2H_2O$$

When combined with naphthol this body gives a bright orange precipitate of benzene-azo-naphthol,

$$C_6H_5N:N.Cl + \underset{\text{(Naphtholate of soda)}}{C_{10}H_7ONa} = \underset{\text{(Benzene-azo-naphthol)}}{C_6H_5N:NC_{10}H_6.OH} + NaCl$$

From the above it will be seen that one equivalent of aniline hydrochloride requires one equivalent of nitrous acid for its complete diazotisation ; or using nitrite of soda and hydrochloric acid, one equivalent of each. Thus—

$$C_6H_5NH_2.HCl + NaNO_2 + HCl = C_6H_5N:N.Cl + NaCl + 2H_2O$$

In the same way all monamines require one equivalent of nitrous acid, and therefore the same chemical equation will serve for each if aniline is replaced by quantities which are in the case of monamines identical with their molecular weights. Benzidine and tolidine are both diamines, and consequently their equivalents are *half* their molecular weights. Thus—

93 parts by weight of	Aniline	Mol. wt.	93	require 69 parts $NaNO_2$.
138 ,, ,,	*p*-Nitraniline	,,	138	,, ,, ,,
197 ,, ,,	Aminoazobenzene	,,	197	,, ,, ,,
92 ,, ,,	Benzidine	,,	184	,, ,, ,,
106 ,, ,,	Tolidine	,,	212	,, ,, ,,

and so on for all other mon- and di-amines.

If the free bases are taken in the first instance, an extra equivalent of hydrochloric acid will be required to convert them into soluble salts,

$$\underset{\substack{\text{Aniline.}\\93}}{C_6H_5NH_2} + \underset{\substack{\text{Hydrochloric}\\\text{acid.}\\2\ (36 \cdot 5)}}{2HCl} + \underset{\substack{\text{Nitrite}\\\text{of soda.}}}{NaNO_2} = \underset{\substack{\text{Diazobenzene}\\\text{chloride.}}}{C_6H_5N:N.Cl} + NaCl + 2H_2O$$

It is found that the bulk of the aromatic amines are most easily diazotised in presence of excess of acid and of nitrite. The excess of hydrochloric or sulphuric acid usually amounts to 50 per cent. and prevents the formation of diazoamino compounds, while the excess of nitrite of soda ought not to exceed 10 per cent. of the theoretical quantity, lest the printing rollers should be attacked by the free nitrous acid. Excess of mineral acid hinders, or prevents altogether, the combination of the diazo bodies with naphthols, but the presence of free organic acids has scarcely any effect ; hence, when the diazotisation is complete, the excess of mineral acid is neutralised by the addition of sodium acetate.

Diazo solutions are, in general, extremely unstable, and must, as a rule, be prepared at a temperature not above 5° C.—better at 0° C. In order to keep the temperature down, lumps of ice are freely added to the solution, and also to the finished printing colour or dye liquor. A few amines, such as aminoazobenzene, aminoazotoluene, and the nitrophenetidines may be diazotised at 20°–30° C., and the tetrazo compound of *o*-dianisidine may even be heated to 100° C. without being completely decomposed, but for the most part it is safer to work as near the freezing-point as possible, otherwise the diazo compound decomposes into a tarry mass that is absolutely useless.

Perfect diazotisation is best effected when the salts of the bases are in solution, or in an extremely fine state of division. Some salts, *e.g.* naphthylamine hydrochloride, are only sparingly soluble, and in such cases they can only be used in dilute solution, or when ground up into a perfectly smooth cream ; other bases, like aniline and *p*-nitraniline, are soluble as hydrochlorides, and if pure, yield clear diazo solutions without any trouble. As a rule, however, it is safer to filter the solution after diazotising, especially if it be intended for printing.

Not only are diazo solutions susceptible to elevations of temperature, but they may also decompose spontaneously on standing a few hours. Indeed, the whole process of producing the Azoic colours on the fibre must be got through as quickly as possible if good results are to be obtained.

3. The Development of the Colour.

The development of Azoic colours is brought about either by printing a thickened diazo solution on the naphtholated cloth, or by passing the latter at the full open width through a solution of the diazo body contained in a padding mangle. If the goods are printed, they are dried lightly and at once washed, sometimes soured, and soaped ; if dyed, they are washed and soaped at once, the dyeing, washing, etc., being carried out, as a rule, in a continuous machine. They are then dried and finished as usual. If goods printed in diazo solutions on a naphthol ground are allowed to lie exposed to the air and light, the white unprinted parts become brown, and the whole print is irrevocably spoiled.

Two important features of the Azoic colours are that they can be both resisted and discharged by means of strong reducing agents. In the first case the diazo solution is destroyed by a resist printed on the naphthol-prepared cloth ; while, in the second, the fully developed colour is discharged by a reducing agent printed on in a suitable pattern. Details of these processes will be found in the section on “ Resists and Discharges.”

The Application of the Azoic Colours.

According to the class of work in hand, its style, requirements, and the conditions under which it is to be executed, the Azoic colours may be applied by any of the following methods :—

A.—By printing a pattern in a thickened solution of naphthol and afterwards dyeing in diazo solutions.

B.—By printing a thickened diazo solution on cloth prepared in naphthol.

C.—By padding the cloth in naphthol for plain shades, and then dyeing it up in diazo solutions.

D.—By coupling diazo compounds with certain other compounds containing free amino groups.

E.—By printing on naphtholated cloth certain reducing agents capable of reducing the diazo compounds before they can unite with the naphthol.

F.—By discharging Azoic colour grounds with reducing agents acting under the influence of steam. The grounds for this process are dyed by method C.

Each of these methods has its special uses, and although similar, almost identical, effects can be obtained from A and B on the one hand, and from E and F on the other, each one will be found to possess certain advantages over the others for certain styles of work.

(A) Printing of Thickened Naphthol Solutions on Plain Cloth followed by Development in Diazo Solutions.

This simple method is largely used for imitating the *Red, Black, and White Madder Style*, and gives very good results with paranitraniline and one or two other amines which do not stain the white too much.

The mixtures given below are printed on white cloth and then thoroughly dried, but at a comparatively low temperature to avoid unevenness in the ultimate colour—an unevenness due to the fact that at too high a temperature the naphthols sublime.

I. Naphthol Printing Colour for full shades of Red, etc.

470	grms.	β-naphthol.
30	,,	Shading salt R.
1,000	,,	water.
850	,,	caustic soda 50° Tw.
300	,,	Alizarin oil 25 per cent.
7,350	,,	gum tragacanth 5 per cent.
10,000		

II. Printing Colour for Light Reds or Pinks, etc.

46	grms.	β-naphthol.
4	,,	Shading salt R.
100	,,	water.
85	,,	caustic soda 50° Tw.
30	,,	Alizarin oil 25 per cent.
9,735	,,	gum tragacanth 4 per cent.
10,000		

After printing and drying, develop at once in diazo solutions of any suitable amine, such as—

Paranitraniline for red and pink,
α-Naphthylamine for claret,
Chloranisidine for scarlet,
Paranitro-orthotoluidine for orange,

and various mixtures for browns. Recipes for suitable diazo solutions will be found on page 528.

For the Black and Red style, another naphthol sold under the name of Nigrophor is thickened and printed as above. It yields a good black with paranitraniline, but is not very suitable for use with other diazotised amines.

300	grms.	Nigrophor.
1,500	,,	water.
350	,,	caustic soda 64° Tw.
500	,,	Alizarin oil 40 per cent.
7,350	,,	gum tragacanth 6 per cent.
10,000		

Various shades of chocolate may be produced by adding different amounts of α-naphthol to the β-naphthol printing colours. Thus—

	Medium Chocolate.	Dark Chocolate.
β-Naphthol	40 grms.	25 grms.
α- ,,	8 ,,	25 ,,
Caustic soda 70° Tw.	80 ,,	80 ,,
Water	152 ,,	150 ,,
Gum tragacanth 6 per cent.	720 ,,	720 ,,
	1000	1000

Both these chocolates are developed in diazotised p-nitraniline.

After the development of the colour all goods are well washed and soaped. The addition of a little sodium hypochlorite (soda chemick) to the soap baths improves the whites and imparts a bluer tone to the red.

The foregoing process is extensively practised for the production of red and white kerchiefs, turban cloths, and other dress goods peculiar to the East and the Tropics. The colours thoroughly penetrate the thin soft cloth used for these fabrics, giving an exceedingly good reversible print. Although not much used for sarrie printing, the same process would undoubtedly give satisfactory results with that class of work.

(B) Printing of Thickened Diazo Solutions on Cloth Previously Prepared in Naphthol Solutions.

This method (the exact reverse of the preceding) is perhaps more largely employed than any other, for the simple reason that it is applicable to so many multicolour styles, and that, therefore, it increases the scope of those styles. It allows of the Azoic colours being printed with any *steam colours* that are sufficiently fixed by a short steaming process of 3–4 minutes, and it further allows of a Para red, etc., being employed in combination with some of the raised colours like Iron buff, Chrome yellow, and some of the vegetable colours that are fixed by a run through a solution of bichromate of soda, or, for Iron buff and Manganese bronze, through caustic soda.

In brief, the process is as follows:—(1) The goods are mangle-padded in one or other of the naphthol prepares given below; (2) dried in hot air or over steam-heated cylinders; (3) cooled and printed with the thickened diazo solutions; (4) dried and, if required for other colours in the pattern, steamed for 2 to 4 minutes in the rapid ager, and then fixed in tartar emetic, etc.; (5) well washed, soaped, and dried.

(*a*) Preparing with Naphthol.—Each maker of naphthols recommends certain formulæ for the application of his particular products. Most of these formulæ require to be modified for use on the large scale; and as they differ from each other in detail only, it would be neither interesting nor profitable to discuss their relative merits. The only suggestions of any real value that have been made with a view to improving the shades obtained, and to increasing the stability of the naphthol solutions, are those which concern the addition of Turkey red oil or castor oil soap (soluble oil) and antimony compounds to the prepares. These substances certainly exert a beneficial effect, and are used whenever there is any doubt as to whether the naphtholated cloth can be printed with the diazo solution at once; and also when the naphtholated cloth has to be dried over metal cylinders or printed by machine.

The following naphthol prepares or groundings have all yielded good results in practice:—

	1.	2.	3.	4.	5.	6.
	grms.	grms.	grms.	grms.	grms.	grms.
β-Naphthol . . .	30	..	47	25	30	26½
β-Naphthol R. . .	..	30	..	..	..	..
α-Naphthol . . .	..	..	..	..	..	3½
Shading salt R. . .	..	..	3	..	..	..
Caustic soda 36° Tw. .	45	60	85	40–50	60–75	60
Turkey-red oil . .	25	25	..	..	25	..
Tartar emetic . .	6	6	10	..	..	..
Tartaric acid . .	7½	7½	12	..	..	..
Boiling water to . .	1000	1000	1000	1000	1000	1000

In some instances it is advisable to replace a portion of the water with gum tragacanth in order to ensure an even impregnation of the cloth. The quantity used varies from 70–80 grms. of a 6 per cent. tragacanth thickening per litre.

No. 1 Prepare.—For all ordinary Azoic reds, clarets, scarlets, and oranges.

No. 2 Prepare.—For very blue shades of Para red, and reds and pinks, from *o*-nitroparaphenetidine and paranitro-orthoanisidine.

No. 3 Prepare.—Same as No. 2, but for stronger colours or on thin cloth.

No. 4 Prepare.—An ordinary prepare for Naphthylamine clarets, and Benzidine and Tolidine chocolates.

No. 5 Prepare.—For same purposes as No. 4. Darker shades.

No. 6 Prepare.—For dull reds with *p*-nitraniline, and dark Naphthylamine clarets.

For light shades of any of the above colours, the prepare is reduced in strength by the addition of extra water. This is, of course, only possible when light shades alone are printed; dark shades require the full quantity of naphthol (2½–5 per cent. solutions). An excess of naphthol, however, does not injure the tone of the lighter colours, but is merely wasted when these alone are printed.

It is almost needless to point out that, if desired, any diazo solution can be printed on any of the above prepares. In fact, Nos. 2 and 3 are largely used for multicolour combinations of the Azoic colours, and are, on the whole, the most important of the series.

After drying, the naphthol-prepared pieces are cooled by passing over a system of rollers, wound on wooden or iron shells or centres into rolls, and are then ready for printing with the diazotised amines.

(*b*) Diazo Printing Colours.—Under proper conditions, the printing of diazo solutions is a comparatively simple matter, requiring no more than a reasonable amount of care; but, as already noted, all such solutions are liable to decompose at the ordinary temperature, or when kept too long before use; and therefore, in order to obtain successful results, it is well to observe the following precautions, which reduce the tendency of the colours to decompose spontaneously:—

(1) All colour should be sent to the printer in tinned or earthenware vessels standing in a wooden tub filled with ice, or with crushed ice and coarse salt.

(2) No more colour should be made than is necessary for the time being; and, as diazo solutions keep longer in presence of free mineral acid, the acetate of soda which is required to neutralise the mineral acid must only be added to the printing colour a few minutes before it is sent in to the printer.

(3) The colour boxes in the printing machine ought to be as small as possible, so that the colour can be constantly renewed with a minimum of loss. They

ought, moreover, to be of tinned copper and double cased, or jacketed, so that the colour can be kept cool by the circulation of cold water between the two casings. A better plan is to have a small box with a double bottom and one double side, sufficiently capacious to allow of broken ice being introduced beneath and around the colour box proper.

(4) For finely engraved and small patterns which take but little colour, or when the particular colour used happens to froth badly, it is advisable to use a doctor box in place of the usual colour box. The advantage of this is that the colour can be renewed at very frequent intervals; and as doctor boxes hold very little, they can be washed out and charged with perfectly fresh colour without any great loss of material. The presence of decomposition products not merely gives a poor, dirty shade, but, worse still, accelerates the rate of decomposition of any fresh colour that is added to replenish the colour box. With large heavy patterns or blotches, the colour is printed before it has time to decompose, but with fine patterns there is always a danger of the decomposition products accumulating in a large colour box.

(5) If decomposed particles of colour are found to adhere to the printing roller, they may be removed by using a brush furnisher. This should be a last resort, however, since thickened diazo solutions are sufficiently prone to froth without any aid from the churning action of a revolving brush furnisher.

(6) To prevent the soiling of the whites by an excess of diazo solution which comes off in the subsequent washing operations, the naphthol grounding or prepare must be a little stronger than is absolutely necessary for the full development of the colour, and it should also be made tolerably alkaline. By these means the diazo compound is completely absorbed, and all danger of dirty whites arising during washing is avoided.

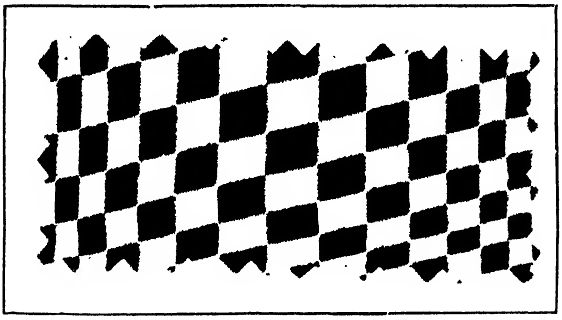
After printing, the pieces should be well dried, but on no account allowed to stand on the drying cylinders, or in the hot-air chamber, otherwise the naphthol on the white unprinted parts of the cloth turns brown.

After-treatment of Printed Azoic Colours.—The printed goods, if they contain none but Azoic colours, are passed quickly through a warm bath of dilute sulphuric acid to remove any surplus diazo compounds that may exist. They are then well washed and soaped, washed again, and dried. If more convenient, a boiling soap bath may replace the acid bath; a hot $\frac{1}{2}$–1 per cent. solution of naphtholate of soda may also be employed instead of the acid. The whites are improved by a light chemicking in the chloring machine, or by the addition of soda chemick to the last soap bath. A better method, however, is to pad the printed and washed goods in a weak solution of sulphoxylate-formaldehyde, then dry and steam.

Goods printed both with Azoic colours and others fixed by steaming are first passed through the rapid ager and then (if basic colours are present) fixed in tartar emetic, well washed and soaped, the operations being conducted in an open soaper.

For blotches and all heavy patterns embodying large masses of colour, gum tragacanth is the best thickening to use with diazo solutions. Smaller patterns, spots, stripes, checks, and parts of multicolour designs, are best printed with mixtures of flour and tragacanth, or of starch and tragacanth (see *thickenings* for proportions), which give a sharper, cleaner impression of the pattern, and are, withal, cheaper. The natural gums, Senegal, Arabic, etc., and the British gums, are rarely used, since they exert a destructive influence on diazo compounds, due to their reducing properties.

The following recipes are taken from practice, and they represent all the more important older Azoic colours used on the large scale:—



Paranitraniline Red (S.C.I.B.).

RED P.N. (Paranitraniline).

36 grms.	paranitraniline.
100 ,,	ice.
100 ,,	hydrochloric acid 30° Tw.
70 ,,	water.

Mix and add quickly—

24 grms.	nitrite of soda 93 per cent.
70 ,,	water.

Stir well, allow to stand 5–10 minutes, and then filter into—

400 grms.	12 per cent. gum-tragacanth thickening.
100 ,,	ice water.
100 ,,	acetate of soda.
1000	

Print on prepares 1, 2, or 3.

The above red is reduced 2 : 1 for heavy engraving, *e.g.* Red P.N. ½.

RED P.N. ½.

2 parts of Red P.N.
1 part of 5 per cent. tragacanth thickening.
On Prep. 1 a Yellow red is obtained.
,, ,, 2 and 3 a Bluish red is obtained.
,, ,, 6 a Brown orange ,, ,, (dull Terra-cotta).

BLUE RED O. (*o*-Nitroparaphenetidine).

73 grms.	*o*-nitroparaphenetidine 25 per cent.
66 ,,	nitrite of soda solution 14½ per cent.
20 ,,	water. Mix, and then add gradually at 20°–25° C. to—
40 ,,	hydrochloric acid 36° Tw.
200 ,,	water. Allow to stand 5 minutes and then filter into—
550 ,,	flour-tragacanth paste.
51 ,,	acetate of soda.
1000	

Print on prepares 1, 2, and 3.

LIGHT PINK O.

100 parts by weight	Blue red O.
260 ,, ,, ,,	4 per cent. tragacanth thickening.
40 ,, ,, ,,	acetic acid 9° Tw.
400	

The acetic acid is only added to neutralise the excess of alkali in the prepare when this pink is printed along with full strength Azoic colours on a strong naphthol ground. Too much alkali is apt to cause irregularities in the colour.

The above red and pink are very stable, as is proved by the fact that ortho-nitroparaphenetidine can be diazotised at 25° C.

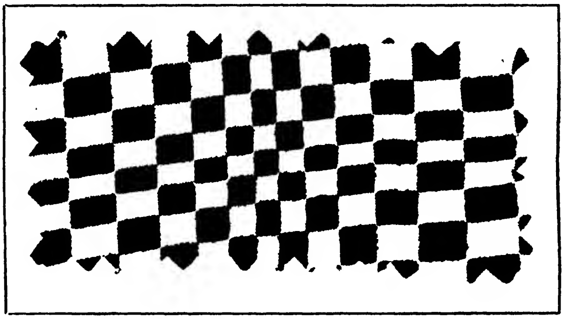
α-NAPHTHYLAMINE CLARET (Claret A.N.).

Stock Naphthylamine Paste:—

36 grms. α-naphthylamine.
93 grms. hydrochloric acid 30° Tw.
171 grms. 6 per cent. tragacanth thickening.

300

Grind to a smooth cream.



α-Naphthylamine Claret (S.C.I.B.).

For use take—

300 grms. Naphthylamine paste.

Add gradually—

20 grms. sodium nitrite 93 per cent.
50 ,, water.
100 ,, finely broken ice. Allow to stand and filter into—
425 ,, 4 per cent. tragacanth thickening.
30 ,, benzine.
75 ,, acetate of soda.

1000

Print on prepares 1, 2, 3, 4, 5, or 6 according to circumstances. For the 3 per cent. prepares, Naphthylamine claret 1/3 may be used for ordinary work.

Naphthylamine hydrochloride and Naphthylamine salt S. are both articles of commerce, and may replace the base in the preparation of the printing colour if the proportions are altered in accordance with the differences in molecular weight.

SCARLET C.A. (Chloranisidine).

25 grms. Chloranisidine salt M.
150 ,, water.
200 ,, ice.
25 ,, hydrochloric acid 36° Tw. Add gradually, whilst stirring—
8·25 ,, nitrite of soda 93 per cent.
50 ,, water. Allow to stand 15 minutes and then filter into—
506·75 ,, 6 per cent. tragacanth thickening.
35 ,, acetate of soda.

1000

Print on prepare 1.

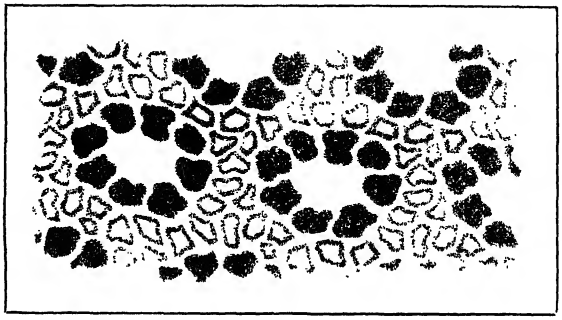
ORANGE N.T. (Orthonitro-paratoluidine).

30	grms.	orthonitro-paratoluidine.
200	,,	hot water.
56	,,	sulphuric acid 61½° Tw. Dissolve, cool, and add—
100	,,	ice, and then at 0°–5° C.—
60	,,	nitrite solution 29 per cent.

Stir well, allow to stand 20 minutes, and then filter into—

54	grms.	water.
40	,,	acetate of soda.
460	,,	6 per cent. tragacanth thickening.
1000		

This colour, reduced to contain 20–25 grms. of nitrotoluidine per kilo., is printed on naphthol prepares 1, 2, or 3. Paranitro-orthotoluidine used as above gives a somewhat brighter orange.



Orange M.N. (S.C.I.B.)

ORANGE M.N. (Metanitraniline).

28 grms. metanitraniline.
200 grms. boiling water.
53 grms. hydrochloric acid 30° Tw.

Dissolve, cool, add first—
150 grms. ice, and gradually—
52 grms. nitrite solution 29 per cent.

Allow to stand 20 minutes, then add water to make up to 500 grms.

For use take 500 grms. diazo solution above.

500	grms.	diazo solution above.
460	,,	6 per cent. tragacanth thickening.
40	,,	acetate of soda.
1000		

Print on any 3–5 per cent. naphthol prepare. For the weaker prepare, the colour used is generally Orange M.N. ¼.

AZO PINK B.B.

A	13	grms.	Azo pink 2 B. base.
	36	,,	water.
	16	,,	hydrochloric acid 30° Tw.
B	50	,,	ice.
	100	,,	cold water.
	30	,,	13 per cent. nitrite solution.

Add B to A gradually, allow to stand 10 minutes, and then filter into—

715	grms.	6 per cent. tragacanth thickening.
20	,,	benzene.
20	,,	sodium acetate.
1000		

For red take 26 grms. per kilo. For paler pink take 5–10 grms. per kilo. Print on prepares 1, 2, 3, or 5. In reducing strong shades to pinks add a little acetic acid (say 2½–5 per cent.) to the reducing paste.

CHOCOLATE T. (Tolidine).

17	grms.	Tolidine base.
200	,,	water.
52	,,	hydrochloric acid 30° Tw.

Boil till dissolved, cool, and add first—

150	grms.	ice, and then gradually at 0° C.—
92·8	,,	nitrite solution 13 per cent.

Allow to stand 10–15 minutes, and then filter into—

440	grms.	8 per cent. tragacanth.
48·2	,,	acetate of soda.
1000		

Print on any naphthol prepare of suitable strength (3 per cent.).

CHOCOLATE B. (Benzidine).

Benzidine chocolate is prepared exactly like Tolidine chocolate, except that 14·5 grms. of Benzidine base are taken in place of the 17 grms. of Tolidine; the quantities of acid and nitrite of soda remain the same in both cases.

The shades given by tolidine and benzidine are almost identical. The former is generally preferred on account of its slightly greater fastness to light.

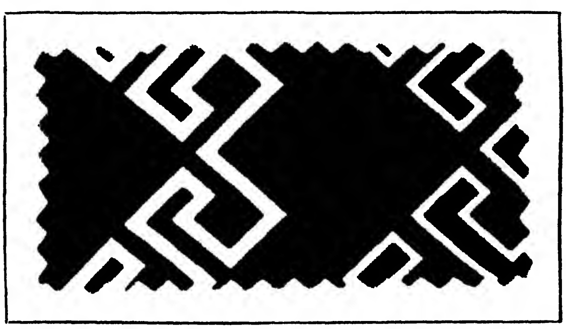
RED N.A. (Paranitro-orthoanisidine).

16·8	grms.	paranitro-orthoanisidine.
150	,,	water.
30	,,	hydrochloric acid 36° Tw. Add gradually at 0° C.—
26	,,	nitrite solution 290/1000.
100	,,	cold water.
84	,,	ice. Allow to stand 10 minutes, then filter into—
500	,,	6 per cent. tragacanth thickening.
25	,,	acetate of soda.

Make up to 1000

Print on prepares, 1, 2, or 3 (1 : 1).

Red N.A. gives a fine red with a beautiful bluish " reflet " ; but it is not so blue in tone as Blue red O., nor so yellow as Para red. For high-class prints on mercerised sateen it is a most useful colour, because it withstands the action of hot steam much better than Para red, which is always more or less dulled if steamed before the naphthol is washed out of the cloth—an operation that it is impossible to perform before steaming when mordant or basic colours or Indigo, etc., are printed in combination with Azoic colours produced on the fibre. At the same time Para red yields excellent results if properly handled, but its shade is generally too yellow for the requirements of the home trade markets of Western Europe.



Paranitro-orthoanisidine Red (I.G.).

BLUE A.N. (Dianisidine).—

12·5	grms.	Dianisidine base.
50	,,	hot water.
18	,,	hydrochloric acid 30° Tw.

Beat into a paste, and then add first—

357	grms.	cold water (melted ice), and then at 0° C.—
62·5	,,	nitrite solution 13 per cent. $NaNO_2$.

Allow to stand 15 minutes, and then filter into—

465	grms.	6 per cent. gum-tragacanth thickening.
35	,,	copper chloride.
1000		

Instead of Dianisidine base (12·5 grms.) there may be used—

16·5 grms. Dianisidine salt and 14 grms. HCl in place of 18 grms.

20·5 grms. Dianisidine salt 80 per cent. paste and 14 grms. HCl in place of 18 grms.

Blue A.N. is printed on a naphthol prepare containing the requisite quantity of acetate of soda to neutralise the free mineral acid in the colour. Thus:—

3 per cent. NAPHTHOL PREPARE.

30	grms.	β-naphthol or Naphthol D.
700	,,	water.
60	,,	caustic soda 36° Tw.
20	,,	sodium acetate.
50	,,	Turkey oil 40 per cent.
140	,,	2 per cent. tragacanth thickening.
1000		

Without chloride of copper, dianisidine gives, on β-naphthol, a dull violet shade of no practical value; on Naphthol A.S. a full and fast blue is obtained.

Mixtures of the diazo compounds of benzidine or tolidine with Dianisidine blue (without copper) give various tones of deep black on β-naphthol-prepared cloth. Many of the Azoic blacks of commerce consist of such mixtures.

The preparation of diazo printing colours can be effected without the use of ice if the amino base and the acid are thickened together and mixed with a second paste containing the nitrite. One example will suffice to illustrate this method of working.

α-NAPHTHYLAMINE CLARET (without ice).

I.	36	grms.	naphthylamine base.
	171	,,	6 per cent. gum-tragacanth thickening.
	93	,,	hydrochloric acid 30° Tw.

Grind to a smooth paste in a mill.

II.	20	grms.	sodium nitrite cryst. 93 per cent.
	50	,,	water.
	525	,,	4 per cent. tragacanth.

Mix I. and II. together, and just before printing add—

30	grms.	benzine.
75	,,	acetate of soda.
1000		

Print on any β-naphthol prepare. The presence of the thickening material retards the rate of diazotisation, and the reaction takes place regularly and

evenly. At the same time it is not advisable to dispense with ice in warm weather, since all diazo compounds are very sensitive to heat—that is to say, all diazo compounds prepared according to any of the foregoing directions.

The Azophor colours—a series of stable diazotised aromatic amino-bases—are now obsolete. They have been replaced by the Fast Colour salts (see Naphthol A.S.).

As is well known, it is impossible to obtain a black when any of the ordinary Aniline blacks are printed on naphthol prepares, even when they are made sufficiently acid to more than neutralise the caustic soda in the prepare. M. Richard, however, found that a mixture of aniline and para-aminodiphenylamine (Diphenyl black), when printed on naphtholate of soda and steamed for 2–3 minutes in the rapid ager, gave a rich, full black, very deep, and much faster than any other black.

The only difficulty with this black is that it is apt to have a light-coloured edge wherever it fits closely to a printed Azoic colour, or when it is printed alone on naphtholated cloth which is afterwards dyed in diazo solutions. This light edge, or aureole, is due to the running of the acids in the colour, and may be avoided by reducing the acidity, and by adding a little China clay to the thickening.

Aniline Blacks on Naphthol Prepares.

	I.	II.
	grms.	grms.
Diphenyl black oil D.O.	45	..
„ „ base I.	..	16
Aniline salt	45	56
„ oil	..	12
Paraphenylenediamine	..	5
Acetic acid 9° Tw.	50	56
Lactic acid 50 per cent.	50	..
Hydrochloric acid 34° Tw.	14	..
Thick acid starch-tragacanth paste	612	..
6 per cent. gum tragacanth	..	560
China clay paste 50 per cent.	..	100
Sodium chlorate	35	30
Water	90	70
Copper sulphide 30 per cent. paste	15	20
Water	15	40
Aluminium chloride 52° Tw.	19	20
Vanadium solution 1 per cent.	10	15
	1000	1000

Print, along with any Azoic colour, on Naphthol prepares 1, 2, or 3; pass through the rapid ager; wash well and soap. Black II. (Noelting and Lehne) gives a fine, deep colour, free from white edges, and may be used for either printed or dyed styles.

The Logwood blacks printed on naphthol-prepared goods are limited to such as are readily fixed by a short steaming, or even on drying in hot air—*e.g.* the Logwood iron blacks. Any Logwood iron black that is suitable for Turkey-red discharge work is well adapted to printing in combination with Azoic colours on naphthol prepares. The one given (p. 518) has been worked out specially for this class of work; it yields a very good black, gives a sharp, clean impression of the pattern, and requires no steaming for its fixation. A run through bichromate of potash improves both its shade and fastness to soaping

when the goods are not steamed; but when steamed, it is sufficiently fast without any after-treatment beyond soaping and washing.

One great advantage of this Logwood black over Azoic blacks is, that it gives excellent results with rollers engraved in stipple, a quality which can scarcely be claimed for any other black on naphtholate of soda.

BLACK J. (on Naphthol Prepares).

90	grms.	Hematine (dry Logwood extract).
300	,,	water.
100	,,	acetic acid 9° Tw. Dissolve and add—
100	,,	starch.
40	,,	British gum.
100	,,	water.
105	,,	potassium sulphite 90° Tw.
20	,,	olive oil. Boil and add—
105	,,	copperas.
140	,,	water (boiling). Boil for 10 minutes longer and then cool.
1100 = 1000 after boiling.		

Print on any naphthol prepare. Goods printed with Azoic colours and Black J. alone are not steamed, but passed immediately through a ½ per cent.-1 per cent. solution of bichromate at 40°-50° C., well washed, soaped, washed, and dried. If mordant and basic colours are added to the colour combination, the goods are steamed for 2-4 minutes, fixed in tartar-emetic, washed, soaped, and washed, the chroming being omitted. All operations of chroming, fixing, washing, and soaping are best and most conveniently carried out in the continuous open soaper.

Direct Production of Para Red on the Fibre.—The production of Para red on the fibre without the necessity of previously preparing the cloth in β-naphthol has been the subject of many investigations; and though the problem has been solved successfully, the processes suggested are but little used now that colours of the Rapid Fast type are available.

Nitrosamine red supplies one of the solutions. It comes into the market in the form of a paste containing the sodium compound of the nitrosamine $\left(C_6H_4\begin{cases}NO_2\\ N:NONa\end{cases}\right)$ obtained by adding diazotised paranitraniline to excess of caustic soda, and as such is incapable of coupling with β-naphthol. The printing colour is made by mixing caustic soda, β-naphthol, nitrosamine red, acetate of soda, and tragacanth thickening, and it is printed on white unprepared cloth. After printing, the goods are gently dried and exposed to the air for a few hours, and then passed through a bath of dilute sulphuric acid, washed, and dried. The combined action of the carbonic acid of the air and the sulphuric acid results in the formation of Para red, so that the process is capable of varied application in combination with suitable colours.

One of the best contributions to the study of Nitrosamines is cited in the *Journal of the Society of Dyers and Colourists*, August 1909, from which the following particulars are taken. The nitrosamine there mentioned will serve to illustrate the principles of the direct production of Azoic colours on the fibre. It consists of a comparatively stable diazo derivative of paranitro-orthoanisidine, and is prepared as under:—

5000	grms.	boiling water.
2530	,,	paranitro-orthoanisidine.
6000	,,	hydrochloric acid 30° Tw. Dissolve, cool, and add—
7000	,,	ice, and then rapidly—
1125	,,	nitrite of soda, dissolved in a small quantity of water.

The diazo solution is allowed to stand 2–3 hours, and is then mixed with 16 litres of caustic soda 36° Tw.; the voluminous microcrystalline green mass of the nitrosamine compound is collected and pressed so as to yield 8500 grms. of paste. It does not undergo decomposition for some days, especially in presence of a little caustic soda; it is easily soluble in water, from which it may be obtained in a crystallised form by salting out; and it does not combine with phenols in presence of alkali. This nitrosamine of *p*-nitro-*o*-anisidine is applied to cotton fabrics in exactly the same manner as the older nitrosamines and yields a brighter red, especially with aluminate of soda, which protects it from the action of acids in the atmosphere. The printing paste recommended by Dziewonski, the author of the paper from which the above information is derived, is made up as follows:—

Red from Nitrosamine.

30	grms.	β-naphthol.
25	,,	caustic soda 76° Tw.
35	,,	sulphoricinoleate of soda 50 per cent.
75	,,	aluminate of soda 15° Tw.
50	,,	warm water.
75	,,	Nitrosamine paste.
220	,,	tepid water.
10	,,	acetate of soda.
480	,,	neutral tragacanth thickening 8 per cent.
1000		

Print on white unprepared cloth, dry, expose to the air for a few hours, pass through sulphuric acid (20 grms. H_2SO_4, 168° Tw. per litre) at 65° C., wash well, soap, and dry. A treatment in boiling water may replace the acid bath.

For resist effects under Aniline black a similar paste is used, but containing an extra amount of acetate of soda. It is printed on white cloth, and the red is developed by a 6 hours' exposure in a warm hanging room at a temperature of 30°–40° C. The Aniline black is then printed over it in a cover pattern, or with a pad roller, and the black is developed in the usual way by a run through the rapid ager, followed by chroming, washing, soaping, and drying.

As a discharge on Indigo, the nitrosamine of paranitro-orthoanisidine is particularly suitable, since it gives a first-rate red by the direct application of nitrosamine, naphthol, and chromate of soda. The presence of zinc, aluminium, and chromium salts or hydroxides exerts a beneficial influence on the brightness and fastness of the red. No more caustic soda should be employed than is sufficient to neutralise the chromic acid in the bichromate of soda, and to prevent the coupling of the nitrosamine with the naphthol. The indigo-dyed cloth is prepared with a solution containing 2 per cent. boric acid and 3 per cent. acetate of ammonia. After printing, the goods are steamed 2–6 minutes in the rapid ager, then passed through the ordinary cutting bath of oxalic and sulphuric acids at 70°–75° C., and finally well washed and dried.

Although not noted in the original paper, it is probable, in view of the fact that zinc compounds improve the red, that the above nitrosamine would lend itself admirably to the production of red resists under Aniline black covers and pads by Pluzanski's process, and therefore, in combination with Basic colours, Chrome yellow and Prussian blue.

Another process relying on the use of the ordinary nitrosamine of paranitraniline was patented by The Calico Printers' Association and by E. A. Fourneaux in 1907 (No. 704, 1907). In this process the calico is printed with a mixture of β-naphtholate of soda, castor oil soap, nitrosamine, and an acid

ester (such as acetine) or monochlorethyl alcohol, both of which split up by hydrolysis, and by thus yielding free acid convert the nitrosamine into the acid diazo compound, which at once combines with the naphthol to form Para red. The following is one of the examples given :—

PRINTING COLOUR.

25	grms.	β-naphthol.
25	,,	castor oil soap (60 per cent. fatty acid).
50	,,	caustic soda 36° Tw.
135	,,	water.
550	,,	gum-tragacanth thickening.
60	,,	Glauber salt. Before use add—
15	,,	chlorethyl alcohol.
15	,,	neutral acetine (42 per cent. $C_2H_4O_2$).
125	,,	Nitrosamine paste 25 per cent.
1000		

Print on plain bleached cloth, allow to lie 24 hours, and then age or wash according to the necessities of the case.

Further improvements relating to the production of Paranitraniline red on the fibre in one operation formed the subject-matter of a second patent taken out by the Calico Printers' Association and E. A. Fourneaux (Eng. Pat. No. 765, 1907).

These improvements consist essentially in printing a thickened mixture of Nitrosamine paste and the magnesium salt of 2-naphthol-1-sulphonic acid (β-naphthyl sulphonate), with or without the addition of Turkey-red oil, etc., on white bleached calico, and then, after drying, steaming the goods for 1 minute without pressure. During the steaming, the nitrosamine reacts with the 2-naphthol-1-sulphonic acid, with the formation of Para red, the sulpho-group being eliminated.

This process allows of Para red being associated with almost any class of colouring matter, including Aniline black, Indigo, and mordant dyestuffs like Alizarin blue, Modern blue, violet, and yellow, and others that can be fixed by a short steaming. No previous preparation of the cloth with naphthol is necessary, since the printing colour contains all the elements essential to the production of the red, and thus a considerable economy is effected in time, labour, and material.

The following is an example of the above process :—

RED PRINTING COLOUR.

A	36	grms.	magnesium sulphate.
	100	,,	tragacanth thickening.
	125	,,	Nitrosamine red paste.
	181	,,	water.
B	400	,,	tragacanth thickening.
	20	,,	ricinoleïc acid.
	20	,,	turpentine.
	15	,,	neutral acetine.
	103	,,	basic magnesium 2-naphthol-1-sulphonate (obtained by stirring the normal salt with excess of magnesium hydrate until the solution contains about 364 grms. of the basic salt per litre).
	1000		

Shortly before printing, mix A and B together, print on plain white calico, dry, steam for one minute without pressure, wash, soap, and dry.

The addition of 1 grm. of urea per kilogramme of printing colour is stated to improve the fastness to steaming.

Azoic Colours with Steam Colours.

The employment of steam colours with Azoic colours is of special interest, since it permits of an immense variety of multicolour effects being obtained, and thus extends the resources of the calico printer. The colours most frequently employed for this purpose are the basic aniline colours fixed with tannin, and mixed with citric and tartaric acids to neutralise the alkalinity of the naphtholate of soda, as well as to preserve the brightness of the shades. But certain mordant colours are also applicable, and these are most useful for the production of dark olives, myrtles, navy blues, and greys. Amongst the most important may be mentioned—Modern and Ultra series of chrome colours, Azochromine, Betanol blue, the bisulphite compounds of Alizarin blue, Cœruleïn, and also Persian berries extract, with chromium or tin mordants. All these can be fixed by a short steaming in the rapid ager, and are remarkably fast to soaping.

Chrome yellow and Iron buff are occasionally associated with Azoic colours, but they are not in much demand, and are never used with steam colours.

The following recipes will illustrate the general methods of work in the combined Azoic and steam colour styles:—

Basic Colours.

Except for the addition of extra acid and a small quantity of stannous chloride to preserve the colour from being soiled by the "scumming" of the diazo solution, the Basic colours are made up in the same way as for the ordinary steam style. The following may serve as examples:—

	Pink.	Yellow.	Green.	Blue.
	grms.	grms.	grms.	grms.
Rhodamine 6 G. extra	10	..	..	..
Thioflavine T.	..	20	20	..
Brilliant green	..	..	10	..
New methylene blue N.	..	..	..	25
Acetic acid 9° Tw.	200	200	200	200
Citric acid	25	25	25	25
Starch	120	100	100	100
4 per cent. tragacanth thickening	340	300	300	300
Water	105	155	145	190
Boil, cool, and add—				
Tannin 50 per cent. solution	200	200	200	160
Tin crystals (optional)	5–10	5–10	5–10	5–10
	1000	1000	1000	1000

Print on prepares 1, 2, or 3; steam 2–3 minutes; fix in tartar-emetic and chalk; wash well, soap, wash, and dry. A pattern illustrating this method, but printed on Naphthol A.S., will be found in the section on Naphthol A.S.

Mordant Colours.

For quiet, fast colours, more suited to the home trade markets, the mordant colours are both the best and the simplest to apply on naphthol-prepared cloth. Their range includes navy blues, light blues, dark myrtle green, olives, greys, and yellows, and certain bright but not very fast chrome reds. The Alizarin pinks, etc., are altogether useless, since they require prolonged steaming for their full development and fixation. Moreover, they are unnecessary, as bright pinks, salmons, scarlets, reds, etc., all occupy an important position in the list of Azoic colours themselves.

Typical examples of mordant colours used on the large scale for printing in combination with Para red and other Azoic colours are given below. They may be, and are, used for ordinary steam styles without any modification whatever.

Yellow	75 grms.	Persian berries extract 48° Tw.
	75 ,,	Quercitron bark extract 48° Tw.
	775 ,,	acid starch-tragacanth paste.
	75 ,,	acetate of chrome 30° Tw.
	1000	

Blue	30 grms.	Brilliant Fast Cyanine R. (Durand & Huguenin).
	820 ,,	acid starch paste.
	150 ,,	acetate of chrome 23° Tw.
	1000	

Olive	4 Yellow.
	1 Blue.
Grey	1 Yellow.
	4 Blue.

Navy Blue	30 grms.	Ultra violet B. (Sandoz).
	4 ,,	Setoglaucine (Geigy).
	100 ,,	acetic acid 9° Tw.
	300 ,,	3 per cent. tragacanth thickening.
	100 ,,	starch.
	266 ,,	water.
Boil, cool, and add—		
	150 grms.	acetate of chrome 15° Tw.
	50 ,,	50 per cent. tannin solution.
	1000	

Myrtle (*Dark Bottle Green*)	60 grms.	starch.
	200 ,,	water.
	230 ,,	3 per cent. tragacanth thickening.
	120 ,,	Persian berries extract 48° Tw.
	75 ,,	Logwood extract 48° Tw.
	30 ,,	olive oil.
Boil and add—		
	20 ,,	Brilliant green.
	125 ,,	acetic acid 9° Tw.
Boil a little longer; then cool and add—		
	100 grms.	acetate of chrome 15° Tw. (pure).
Stir well and then add—		
	40 ,,	50 per cent. tannin solution.
	1000	

This Myrtle gives a dark shade of green equal in depth to a Navy blue. In combination with Para red, Naphthylamine claret, Navy blue, and Black J., it is extensively used for the production of rich plaid checks on flannelettes.

After printing, the goods are steamed 3–4 minutes in the rapid ager, passed at once through tartar-emetic, and then washed and soaped.

Reduced with starch paste or tragacanth, the above myrtles give useful and pleasing shades of a bluish-green, which may be toned to any extent by the addition of yellow.

Colour combinations containing Navy blue, Myrtle, and any of the brighter colours, always require steaming and fixing in tartar-emetic ; those containing Azoic colour and Black J. only are merely dried after printing, and then passed directly into a chrome bath—the black fixes perfectly without any steaming, and is, in fact, fast enough to withstand a severe soaping. Diphenyl black must be steamed as is usual for all steam colours.

Azoic Colours printed with Vat Dyestuffs.—The Azoic colours may also be printed in conjunction with most of the Vat dyestuffs. In this case the naphthol-prepared goods are printed with the ordinary Indigo, Ciba colour, or Indanthrene colour printing pastes (alkali-hydrosulphite pastes), along with any desired diazo solution ; they are then steamed in the rapid ager at 102° C., passed at once into a copious supply of cold running water until the vat dyes are re-oxidised, then soured (if need be) with sulphuric acid at ½° Tw., and finally well washed and soaped (for Ciba colours, at the boil).

Azoic Colours with Lead Yellow and Iron Buff.—These are simple styles, used only for handkerchiefs, etc., for the Eastern markets. Usually a black is printed at the same time, and, if the style is not very tasteful, the colours are at least very fast.

(*a*) For *Yellow*, the naphthol prepare may contain 2½ per cent. of sulphate of soda. The yellow consists of a thickened solution of basic lead acetate, identical with the *Madder* (*lead*) *yellow* already described. After printing, the goods are passed through a warm bath of dilute sulphuric acid ¾°–1¼° Tw., or through an acid solution of sulphate of soda (20 per cent. solution). They are then well washed and raised yellow in bichromate of soda as described for *Madder yellow* (followed by a treatment in lime water if an orange is required), well washed again, soaped, and washed. If Diphenyl black is introduced into the pattern, the goods are steamed in the rapid ager, and the subsequent acid treatment is best carried out with a solution of sulphate of soda, acidulated with acetic acid, or very dilute sulphuric acid. The addition of acid is not absolutely essential, but it improves the whites and helps to remove any excess of diazo solution that has decomposed and formed a dull brownish film over the Azoic colour. Catechu brown has also been used with success in combination with Para red, Toluidine orange, etc. In this case, also, the *Catechu madder brown* (*q.v.*) is employed, and the printed goods (after steaming for black) are passed directly into a combined fixing and developing bath.

Fixing and Developing Bath.

200	grms.	Glauber salt cryst.
5	,,	bichromate of potash.
1000	,,	water.

Work the goods for 20–30 minutes at 60° C. in this solution, then well wash and soap.

(*b*) *Iron buff* in combination with Diphenyl black and Para red is often used for handkerchiefs. The buff is made by thickening an acetate of iron prepared by the double decomposition of copperas and lead acetate.

BUFF F.

500 grms. British gum paste.
500 „ acetate of iron 18° Tw.

1000

Print Buff F., Red P.N., and Diphenyl black on naphthol prepares 1, 2, or 3 ; steam 3–4 minutes in the rapid ager ; and then raise the Buff by passing the printed pieces through caustic soda 4°–5° Tw. at 60° C. ; wash well, and allow the pieces to lie until the dirty olive precipitate of mixed ferrous and ferric hydrates has become fully oxidised to the latter. Wash again and soap.

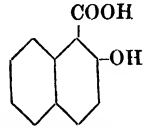
The chromium lake of Alizarin blue withstands the run through caustic soda, and as it fixes well in the rapid ager, it can be employed, with good effect, as an additional colour in the combination. It gives a pleasing slate-like grey, which goes well with red, black, and buff. For a dark chocolate brown Manganese bronze serves admirably. A thickened solution of manganese chloride or sulphate is printed along with the other colours on the naphthol prepare, and the goods are then treated precisely as above. A short run through dilute bleaching-powder is beneficial after the goods have lain a short time ; it completes the oxidation of the manganous hydrate, and brightens the red and white simultaneously.

AZOIC COLOURS WITH SULPHIDE COLOURS.—The printing of Sulphide dyestuffs alongside the Azoic colours calls for no special manipulation of the cloth. After printing, the pieces are steamed in air-free steam for 3–4 minutes, and then passed directly through a series of becks, the first filled with dilute solution of sulphuric acid (1 part acid 168° Tw. to 100 parts water), and the following ones with water, soap, and water respectively. In other respects the process is identical with that for Azoic colours alone.

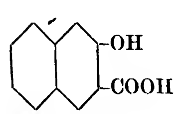
Application of Oxynaphthoic Acids.

The outstanding importance of β-naphthol and its sulphonic acids, not only in the colour-making industry, but also in the printing and dyeing industries for the direct production on the fibre of Azoic colours, prevented, for a considerable time, a general appreciation of the merits of some of its carboxylic acids—the monocarboxylic or oxynaphthoic acids.

According to theory seven isomeric acids of this type are possible, but, up to the present, only two have found any practical application in textile printing, viz. the 2-hydroxy-1-naphthoic, and the 2-hydroxy-3-naphthoic acids.



(M.p. 156° C.).



(M.p. 216° C.).

Of these the latter is much the more important by reason of its property of combining with tetrazo-dianisidine to form a fast blue ; but both possess features of interest to the textile colourist.

2-Hydroxy-1-Naphthoic Acid.—This acid is very unstable, splitting up quantitatively into β-naphthol and carbon dioxide on boiling in water. Its carboxyl group is also easily eliminated by the action of diazo compounds,

and, consequently, when coupled with such bodies, it yields colours identical with those obtained from β-naphthol itself. Unlike β-naphthol, however, its alkaline salts do not sublime on drying or steaming—a property which has been utilised for the fixation of β-naphthol in printing. In other respects it behaves like β-naphthol, is applied in the same way, and produces exactly the same final effect.

2-Hydroxy-3-Naphthoic Acid (m.p. 216° C.).—The use of this acid—generally known as β-oxynaphthoic acid—was first patented in 1891, by Fischesser of Lutterbach (Alsace), for the direct production on the fibre of Azoic colours. The patent covered the use of many amines, and gave as examples the formation of a red from paranitraniline and a blue from dianisidine.

The method was introduced by J. Pokorny (chemist to the above firm) for the express purpose of producing fast blues from dianisidine—a style of great importance, and one which up to that time had not been worked successfully in bulk.

As is well known, β-naphthol when coupled with the tetrazo compound of dianisidine gives an unpleasing dirty violet-blue shade. If, however, the coupling takes place in presence of a copper salt a fine full blue is obtained. This blue, although fast to light and soaping, is, unfortunately, extremely sensitive to the action of dilute acids, so much so in fact that even perspiration destroys it. In order to overcome this defect, which rendered the blue unfit for garment printing, Pokorny suggested the use of 2 : 3-oxynaphthoic acid (m.p. 216° C.) in place of β-naphthol, together with the omission of copper salts from the tetrazo solution of dianisidine. Copper salts are not essential to the production of a fast blue, but their presence certainly increases the fastness to light.

Pokorny's suggestion was adopted by Meister, Lucius, and Brüning, whose Naphthol D. (for Dianisidine blues) consisted of a mixture of β-naphthol, 2 : 3-oxynaphthoic acid, and a naphthol sulphonic acid—a mixture offering no practical advantage over the use of β-oxynaphthoic acid alone.

The process of Fischesser and Pokorny has been confined more or less to the printing of single-colour patterns in dark blue only, and for this style it is excellent. The blues are very fast, and of a rich full shade ; and they lend themselves admirably to the crepon or crimp style, being perfectly resistant to caustic soda. Light blues are not so successful, lacking somewhat in brightness, and, if printed without copper salt, yielding only dull shades of violet. The diazo and tetrazo solutions of most other amines, employed in printing, give useless and loose colours on cloth prepared with β-oxynaphthoic acid, and for this reason the process has failed to become general.

Nevertheless it is capable of considerable extension. For example, although paranitraniline itself only gives a fairly fast reddish brown, yet when printed with an addition of barium chloride and steamed for a few minutes it yields a fairly bright red on subsequent soaping. Other metallic salts may be used for the same purpose : acetate of strontium giving a bright full red, and acetate of calcium a bluish red. Moreover, the Basic colours printed on β-oxynaphthoic acid yield particularly bright shades ; and the necessity for a short steaming to develop the Para red also allows of certain mordant colours being employed. Hence the process, though confined for the most part to the printing of single blues and the blue-red style, is capable of considerable application in other directions. The production of the blue-red style (with Azoic colours) was first rendered possible by Bukowiecke's discovery, in 1906, of the action of barium chloride on the lake obtained by combining paranitrodiazobenzene and 2 : 3-oxynaphthoic acid.

For printing purposes the cloth may be prepared in either of the following solutions:—

	I.	II.
β-Oxynaphthoic acid (m.p. 216° C.)	160 grms.	125 grms.
Caustic soda 86° Tw.	230 ,,	40 ,,
Ricinoleïc acid	230 ,,	..
Castor oil soap 25 per cent. . .	..	600 ,,
Water to .	10,000	10,000

Use at 80°–100° F.

The following colours will serve to illustrate the various groups that are applicable to multicolour patterns:—

Blue: The Dianisidine blue already given (Blue A.N.).
Red: Paranitraniline red, plus 5 per cent. barium chloride.
Basic Colours: Any used for steam work.
Mordant Colours: Modern colours (Durand & Huguenin), Ultra colours (Sandoz), and all other chrome colours and nitroso-naphthols capable of fixation by a short steaming.

After printing, Dianisidine blues alone are simply washed and soaped. Combinations of blue and red, with or without mordant colours, are steamed 3–4 minutes in the rapid ager before soaping; if Basic colours are associated with the above the goods are fixed as usual in tartar-emetic before soaping.

In this way very satisfactory multicolour chintz patterns may be printed on a dark blue or red ground; and by adding barium chloride to other diazo solutions it is possible to introduce further variety into the style. With the exception of Dianisidine blue, however, none of these Azoic colours is as fast to soaping, nor so bright, as the corresponding shade produced on β-naphthol, and this disadvantage has prevented the process from being used for anything but blue (or red) ground prints.

Even in this connection the importance of β-oxynaphthoic acid has declined since the introduction of its derivative Naphthol A.S.—a product which renders unnecessary any special treatment of the diazo solutions, and gives, at the same time, much faster and brighter colours.

(C) The Dyeing of Plain Shades with β-Naphthol Colours.

Plain shades of this description are usually dyed in printworks for subsequently discharging with reducing agents.

The process consists in padding the cloth in one of the naphthol prepares already given; and then passing it, after drying, through the necessary diazo solution contained in the liquor box of an ordinary slop-padding machine. The coupling of the diazo compound with the naphthol takes place almost at once, but, in order to ensure the complete combination of the two bodies, the cloth is given a short run through the air before it enters the washing becks. The whole process is conducted with the cloth in the open width up to the point at which it leaves the washing becks after dyeing in the diazo solution. It may then be washed and soaped in the rope state, since there is no further fear of creases causing unevenness in the shade. A dyeing machine suitable for the purpose is sketched in fig. 81; it is self-explanatory.

The preparation in naphthol is carried out exactly as for printed goods; but, as a rule, it is unnecessary to add antimony salts to the naphtholate of

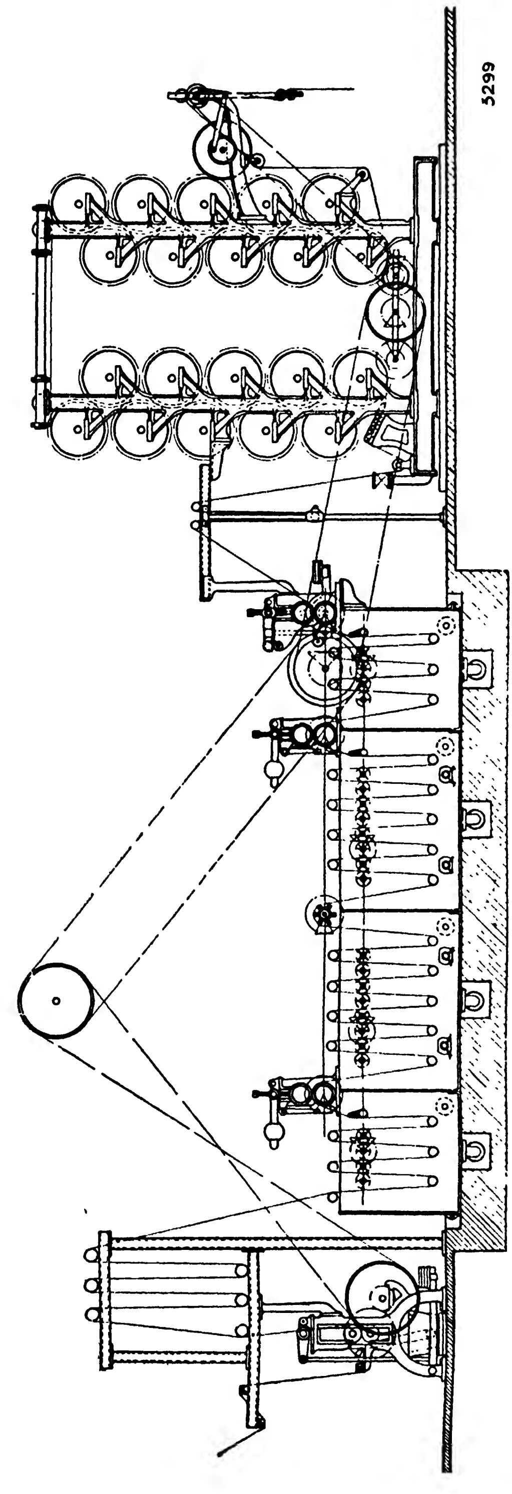


FIG. 81.—Continuous Para red dyeing machine (M. & P.).

soda unless the cloth is to be dried over cylinders, or if it cannot be dyed at once. Two suitable prepares for dyed shades are made up as follows :—

	For Reds.	For Clarets, etc.
β-Naphthol	28 grms.	30 grms.
Shading salt R.	2 ,,	..
Caustic soda 52° Tw.	75 ,,	75 ,,
Turkey-red oil 40 per cent.	25 ,,	..
Water	870 ,,	895 ,,
	1000	1000

The diazo solutions are prepared in the usual way, but without thickening, and are usually of about two-thirds the strength of the corresponding printing colours. Their concentration varies, however, according to the depth of colour required and the strength of the naphthol solution employed. For most purposes the latter rarely exceeds 3 per cent., but if printing is combined with dyeing for the production of two-colour effects, or when two strengths of thickened naphthol solutions are printed side by side with the same object, it may reach 5–6 per cent., and in such cases the strength of the diazo solution must be increased proportionately. The dyeing solutions may be made up as under :—

Paranitraniline Red.

5,000 grms. Paranitraniline C.
20,000 ,, hot water.
25,000 ,, hydrochloric acid 30° Tw.

Dissolve, cool, and add—

26,000 grms. cold water.
50,000 ,, ice.

Then pour in gradually, whilst stirring—

24,000 grms. nitrite solution 13 per cent.

Allow to stand 15 minutes, filter, and add—

74,000 grms. acetate of soda solution $32\frac{1}{2}$ per cent.
1,000 ,, water or ice.

225 kilos.

α-Naphthylamine Bordeaux.

7,000 grms. α-naphthylamine.
26,000 ,, hydrochloric acid 30 per cent.
17,000 ,, hot water.
} Grind to a smooth paste and cool.

68,000 ,, ice.
30,000 ,, nitrite solution 13 per cent.
75,000 ,, acetate of soda $32\frac{1}{2}$ per cent.
2,000 ,, water (or British gum paste).

225 kilos.

The acid in these two mixtures is in a somewhat large excess, but as the acetate of soda is only added immediately before use, and as diazo compounds keep longer in acid solutions, it is an advantage to use a larger quantity, because sometimes the solution has to be prepared some hours before it is actually required.

If desired, the acid can be reduced to 12 kilos. in the red and 13 kilos. in the Bordeaux solutions, but the foregoing quantities have been found to give the most regular work in practice.

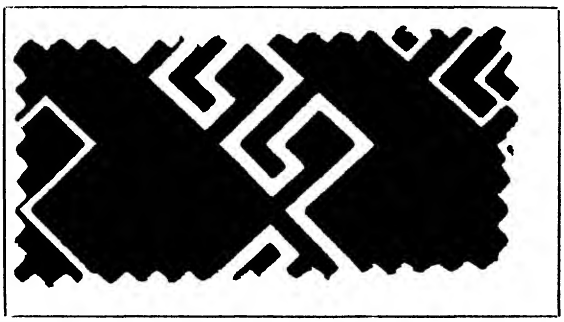
After dyeing, the pieces are well washed and soaped in the open width; then washed and soaped again in the rope form. For reds fast to rubbing, the goods, after the last soaping and washing, are passed through a boiling *dilute* solution of phenol, containing 0·2 grm. of phenol per litre. Para reds are soluble in phenol, and consequently their treatment under the above conditions results in the removal of the surface colour, which only adheres loosely to the cloth and is easily rubbed off in use. Incidentally, too, both the red and the white are improved.

(D) The Coupling of the Diazo Compounds with Colours of the Chrysoïdine Group.

Certain members of the Amidoazo group of dyestuffs combine with diazo compounds to form insoluble, dark brown precipitates. If this reaction takes place on the fibre, the colour obtained is similar to Catechu brown in shade, is very full and rich, and of excellent fastness to light and soap.

In practice, the finest, and therefore the most important, colours of this class are produced by the action of diazotised *p*-nitraniline (paranitro-diazobenzene chloride) on Chrysoïdine and Bismarck brown (Vesuvine). These two dyestuffs are put on the market as Para brown salt G. (Vesuvine) and Para brown salt R. (Chrysoïdine)—names which have been given to them because they are specially adapted to coupling with diazotised para-nitraniline.

The method of producing Para browns on the fibre is practically the same as that employed for the production of Para reds, the only difference being that the cloth, instead of being prepared in naphthol, is printed or padded with solutions of one or other of the Brown salts R. and G. The Brown salt R. gives a redder shade than the G. mark; both are equally suitable for either printing or padding, and both are developed in the ordinary diazo solution used for Para reds. Moreover, the Brown salts can be printed on naphthol-prepared goods, so that when dyed, a brown pattern on a red ground is obtained; and further, as the brown and red are both discharged by the same reducing agents (hydrosulphites), it is possible to obtain white and coloured patterns on a two-colour background.



Chrysoïdine R. (I.G.).

Printing of Para Brown.—The best thickening to use for this purpose is a gum tragacanth-starch paste, or a starch paste alone, according as a blotch or a peg pattern is to be printed.

Dark Brown Printing Colour $2\frac{1}{2}$ per cent.

20	grms.	Chrysoïdine R.
150	,,	acetic acid 6° Tw.
305	,,	water.
50	,,	starch.
475	,,	4 per cent. gum-tragacanth thickening.
1000		

Boil and cool.

Print on white cloth, dry, and develop in diazotised paranitraniline (14 grms. paranitraniline per litre).

Printed thus on plain white cloth, brown and white effects are obtained; while if printed on naphthol-prepared cloth, brown and red effects are produced. After dyeing, the goods are simply washed, soaped, and dried.

Dyeing of Para Brown.—The cloth is first padded in a 1½–2 per cent. solution of Brown salt R. or G.; then dried and developed in diazotised *p*-nitraniline, well washed, soaped, and dried.

The Brown salt padding liquor is usually thickened slightly with tragacanth in order to facilitate the even impregnation of the cloth.

A padding solution, used in practice for dark browns, is made up as follows:—

1½ per cent. Brown Salt for Padding.

15	grms.	Brown salt R. (Chrysoïdine R.).
50	,,	acetic acid 9° Tw.
450	,,	boiling water.

Dissolve, and add—

100	grms.	3 per cent. tragacanth thickening.
385	,,	cold water.
1000		

Pad in any type of padding mangle; dry in hot air or over cylinders, the first few of which are preferably wrapped with calico; and then develop as before in *p*-nitraniline, wash, soap, and dry.

For "two-brown" styles, pad the cloth in a ½ per cent. solution of Brown salt, then print on a stronger colour (say 2–2½ per cent.), dry and develop as usual.

The coupling, *i.e.* the combination of paranitro-diazobenzene with Brown salt takes place much more slowly than with naphthols. After development, therefore, the pieces must be well squeezed between the mangle bowls to express excess of liquor, and then allowed to lie in pile or batch until the reaction is complete. This usually occupies from 15–20 minutes, after which period the pieces may be washed and soaped without any fear of irregularities arising. If washed too soon, the colour is not only weak, but it is apt to be uneven, and in any case full advantage is not taken of the possibilities of the materials used.

Compared with the browns obtained from benzidine and tolidine in combination with metanitraniline, etc., the Para browns possess several advantages. In the first place, they are faster to light; secondly, they are not volatile, even when hot calendered or embossed, and therefore they can be ironed in the laundry without marking off; and thirdly, they yield a pure white with hydrosulphite discharges. These valuable qualities, combined with their rich appearance, their ease of production, and their adaptability to many styles hitherto only possible to produce by roundabout methods, have rendered the Para browns of the utmost importance to the calico printer, and have enabled him not only to introduce many new effects, but also to simplify some of his older processes, and to turn out, at a cheaper rate, a larger quantity and a more varied assortment of high-class goods than he could formerly.

(E *and* F) Resist and Discharge Effects on β-Naphthol Colour Grounds.

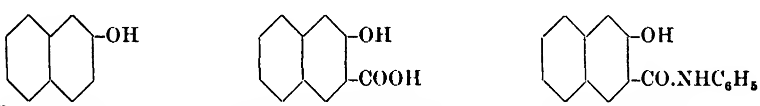
In addition to direct printing, there are two methods of producing white and coloured designs on grounds dyed with Azoic colours: (1) by printing, on the naphthol-prepared cloth, some substance which is capable of chemically changing the diazo compound when the goods are dyed, and thus preventing

the formation of colour on the printed parts ; and (2) by printing on the dyed cloth certain reducing agents which, under the influence of steam, bleach out the colour from those parts of the dyed cloth upon which they are printed. The first of these methods is known as the Reserve or Resist Style, and the second as the Discharge Style. They both form part of a special branch of calico printing ; and as the processes and materials involved in their production are common to other and quite different classes of colouring matters, their description will be deferred to a later section.

Naphthol A.S.

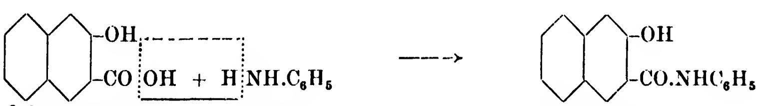
The introduction of Naphthol A.S. in 1912 by the Griesheim Elektron Company was an event of major importance in the world of calico printing and dyeing. It extended the scope of the Azoic colours, opened up entirely new fields for their application and rendered them available in new and fast shades for many styles which, up to then, could not be produced of consistent fastness throughout. Moreover, it led directly to the preparation of a series of valuable analogous compounds, the introduction of which, under the group designation of Naphthol A.S., has revolutionised the application of Azoic colours, and has overcome the disadvantages—looseness to light, poor fastness to rubbing, dull shades on steaming, etc.—which had hitherto attended the use of the β-naphthol colours.

With one exception—Naphthol A.S.-G.—all members of the Naphthol A.S. group are derived from β-naphthol, being in reality substituted β-naphthols obtained by condensing 2 : 3-oxynaphthoic acid with suitable amines : in other words they are all arylamides of 2 : 3-oxynaphthoic acid. The relation between β-naphthol and Naphthol A.S. is illustrated below—



β-Naphthol. 2 : 3-Oxynaphthoic acid. Naphthol A.S.

or



β-Oxynaphthoic acid. Aniline. Naphthol A.S.

from which it is seen that Naphthol A.S. is the anilide of 2 : 3-oxynaphthoic acid. Similarly :

Naphthol A.S.-D. is the *o*-toluidide of 2 : 3-oxynaphthoic acid.
,, A.S.-O.L. is the *o*-anisidide of 2 : 3-oxynaphthoic acid.
,, A.S.-R.L. is the *p*-anisidide of 2 : 3-oxynaphthoic acid.
,, A.S.-B.G. is the diphenetidide of 2 : 3-oxynaphthoic acid.
,, A.S.-B.S. is the *m*-nitranilide of 2 : 3-oxynaphthoic acid.
,, A.S.-T.R. is the 5-chloro-*o*-toluidide of 2 : 3-oxynaphthoic acid.
,, A.S.-B.O. is the α-naphthylamide of 2 : 3-oxynaphthoic acid.
,, A.S.-S.W. is the β-naphthylamide of 2 : 3-oxynaphthoic acid.
,, A.S.-B.R. is the dianisidide of 2 : 3-oxynaphthoic acid.
,, A.S.-G. is diacetoacetic-*o*-tolidide, and is an exception.

In addition to the foregoing, eight or ten other naphthols of similar chemical

structure, *e.g.* Naphthols A.S.-E., A.S.-L.B., A.S.-G.R., A.S.-I.T.R., etc., are in current use and will receive notice later as they occur in the descriptions of processes and styles.

Side by side with the evolution of the Naphthol A.S. series, a number of new bases was introduced, thus increasing enormously the range of the Azoic colours.

The chemical structure of the A.S. Naphthols endows them with properties which render the colours produced by their means much superior in every way to the older " ice " or β-naphthol colours. With the naphthols and bases now on the market it is possible to obtain, directly and without admixture, a complete colour scale comprising all shades of yellow, orange, red, pink, violet, claret, navy blue, pale blue, brown, chocolate, and even black, and, in some styles, green.

These colours possess a beauty, depth, and brilliancy hitherto unknown, and most of them are fast to chlorine and of excellent fastness to washing; many of them, also, are of *very good* fastness to light, and several possess so excellent an all-round fastness as to rank on equal terms with the best Indanthrenes. The reds in particular are much faster than Para red to light and soap, and they neither rub off so much nor are they so sensitive to the staining action of copper and other metals. Many of the Naphthol A.S. colours also resist exceedingly well the detrimental dulling effect of the steaming process and, consequently, may be used safely in multicolour styles from which the more sensitive β-naphthol colours are debarred.

The point which excited most interest in Naphthol A.S. on its first appearance was the fact that it presented a means of obtaining a Dianisidine blue fast to acids. Up to then it had been impossible to produce such a blue either by dyeing or printing; and the same difficulty existed as regards the production of fast Azoic red and blue styles. On β-naphthol " prepares " a fairly fast red was easily obtainable, but only a blue loose to acids and perspiration could be got. On Naphthol D. and β-oxynaphthoic acid " prepares " the blue was much faster, but rather flat, especially in medium shades, while the red was unsatisfactory both in shade and fastness. With Naphthol A.S. these defects are entirely absent. It combines perfectly and rapidly with all the amino-bases in general use, yielding a variety of shades unrivalled for brilliancy and fastness by any other colours of their class. The blue is not only fast to acids and perspiration but, in addition, it is very resistant to the action of boiling soap, soda, bleaching powder, and rubbing, and towards light its dark shades are almost as good as, and its light shades better than, the corresponding shades of Indigo. Moreover, it resembles Indigo closely in tone, being only slightly redder; and as it is capable of being *resisted* and *discharged* it may be substituted for Indigo in many styles for which that dyestuff is used.

Normally Dianisidine blue is much cheaper to print than Indigo. The cost of material is lower, the process shorter, no steaming is necessary, and, if reasonable care is observed in the preparation of the printing colour, no fear of irregularity need arise. After printing, the goods may be allowed to lie a week before soaping off; Indigo prints must be dealt with at once.

Fast red and blue prints similar to those obtained by printing Indigo on Turkey red are easily produced on Naphthol A.S. by two methods of resist. An addition of aluminium sulphate to an Azoic red printing colour causes it to prevent the development of Dianisidine blue when the printed goods are subsequently dyed in a tetrazo-solution of dianisidine. Similarly, an addition of persulphate of ammonia to a dianisidine printing colour destroys the diazo-group of (say) paranitraniline base wherever this latter comes in contact with it, thus producing a blue resist on a red ground, when the goods are finally dyed in paranitraniline dye. The former of these methods (using a

resist red) is still largely used for the standard "blue and red style"; but Dianisidine blue as a ground colour is rapidly being replaced by Variamine blue, which is much faster to light.

The application of the A.S. Naphthols follows closely the lines of that of β-naphthol and, like all Azoic colour operations, it calls for careful attention to detail. In the preparation of the naphthol solutions, and of the printing colours, it is important to observe the correct proportions of the various ingredients, as slight differences frequently cause great irregularities.

Two points call for special attention: (*a*) the substantivity of the A.S. naphthols, which act towards cotton, etc., like direct dyestuffs, being in this respect totally unlike β-naphthol, which has no affinity for the fibre; (*b*) the drying of the padded naphtholated cloth.

The *substantivity* of the A.S. Naphthols is greatest in the cold and diminishes as the temperature is increased. The effect, however, is scarcely noticeable in padding if a small padding box, frequently replenished, is used and if the padding liquor is kept hot. The temperatures most suitable vary with different naphthols and with the speed of the padding mangle, but once established they must be strictly adhered to in order to ensure regular results. At the same time one standard temperature may be adopted so long as it is high enough to give uniform impregnation with the most strongly substantive of the naphthols in use; it will not then injure the least substantive nor affect its dyeing properties.

The *drying* of goods impregnated with (or prepared in) solutions of Naphthol A.S. is an important factor in promoting uniformity of shade in printing and dyeing. Unlike goods prepared with β-naphthol, those prepared with naphthols of the A.S. group must be dried at a comparatively high temperature and as rapidly and evenly as possible. The drying is best carried out in a hot flue at a temperature of 165°–175° F. If the goods are dried at too low a temperature the naphtholate of soda on the cloth splits up into free Naphthol A.S. and caustic soda, with the result that, on coupling, weak and thin shades are obtained. In order to overcome this tendency of the naphtholate to hydrolyse on damp prepared cloth, it is essential that the drying proceed rapidly and that the hot flue be heated *uniformly* throughout. If one side (or edge) of the cloth be dried more quickly than the other, owing to running through a warmer part of the chamber, that side will dye up darker than the other or, if printed, will give a darker pattern; also, to some extent, a similar defect will develop if the upper and lower parts of the drying chamber are not heated to the same temperature. In modern hot flues, such as that illustrated on Plate XIV, these difficulties are eliminated, provision being made, by means of trunks and perforated pipes between the laps of cloth, to distribute the hot air at a regular temperature uniformly throughout the length, breadth, and height of the drying chamber.

The drying of padded Naphthol A.S. prepares may also be effected on steam-heated cylinders, provided the cylinders are not heated too strongly. With a 3-bowl padding mangle giving an expression of 80–100 per cent., an adequate drying can be obtained on a 16-cylinder drying machine with heating steam at a pressure of 12–15 lbs. per square inch. The cloth must be threaded over the cylinders in such a way that each side comes alternately into contact with the heated cylinders, and so that *both* sides are dried equally and rapidly. If cloth intended for dyeing (for discharge and resist styles) is first dried on *one* side only, as is the case with some types of cylinder drying machines, the dyeing on each side will be of different shades, that on the side which was first dried being much the darker of the two. For this reason also the use of cylinder drying machines with only two or three very large cylinders is not to be recommended.

After drying, the prepared pieces are at once wound on a wooden centre or "shell" ready for printing or dyeing; or, if not required immediately, they are rolled into bundles and wrapped up in cloth covers to protect them from moisture, acid fumes, and the action of light. They are not liable to turn brown in storage, but if kept too long the naphthol is more difficult to wash out than with freshly prepared pieces.

Apart from these differences in padding and drying, the general operations connected with the application of Naphthol A.S. are the same as those employed for β-naphthol; the same machinery is used, and what has already been said respecting *preparation of the cloth*, *diazotising*, and *development of the colour* applies equally well to Naphthol A.S. colours.

Many new amino-bases, and stable diazo salts of these bases, have been brought into use for the production of fast Azoic colours, and as most of them were not previously used on β-naphthol prepares, a list of the more important is given below:—

Fast Yellow G.C. base	Hydrochloride of *o*-chloraniline.
,, Orange G.C. base	*m*-Chloraniline.
,, ,, R. base	*m*-Nitraniline.
,, ,, G.R. base	*o*-Nitraniline.
,, Scarlet G. base	4-Nitro-2-aminotoluene.
,, ,, G.G.S. base	2:5-Dichloraniline.
,, ,, R.C. base	Hydrochloride of 4-nitro-2-aminoanisole.
,, ,, T.R. base	,, ,, 6-chloro-2-aminotoluene.
,, Red B. base	5-Nitro-2-aminoanisole.
,, ,, K.B. base	Hydrochloride of 4-chloro-2-aminotoluene.
,, ,, R.C. base	,, ,, 5-chloro-2-aminoanisole.
,, ,, R.L. base	5-Nitro-2-aminotoluene.
,, ,, G.L. base	3-Nitro-4-aminotoluene.
,, ,, 3 G.L. base	2-Nitro-4-chloraniline.
,, ,, T.R. base	Hydrochloride of 5-chloro-2-aminotoluene.
,, Garnet G.C. base	,, ,, 2-aminoazotoluene.
,, ,, G.B.C. base	,, ,, *m*-nitro-*o*-phenetidine.
,, Blue B. base	Dianisidine.
,, ,, B.B. base	1-Amino-2:5-diethoxy-4-benzoylaminobenzene.
,, ,, R.R. base	1-Amino-2:5-dimethoxy-4-benzoylaminobenzene.
,, Black B. base	Mixture of bases.
,, ,, L.B. base	*o*-Phenetolazo-α-naphthylamine.
,, Violet B. base	3-Amino-4-methoxy-6-benzoylaminotoluene.
Variamine blue B. base	4-Ethoxy-4′-aminodiphenylamine.

Many combinations of these bases with various A.S. Naphthols yield extremely fast shades, but as demands for increased all-round fastness become more insistent, constant additions are being made both to the naphthols and the bases, and probably the weaker members of both will eventually be dropped. Amongst the recent additions are: Fast red base I.T.R., Fast orange R.D., Fast Corinth Salt V. and L.B. base—all of which give bright shades of increased fastness in combination with appropriate naphthols.

In diazotising the foregoing bases, those which are soluble in dilute hydrochloric acid have the solution of nitrite of soda added to them, as already described for paranitraniline, α-naphthylamine, etc.; on the other hand, those bases which are not soluble are first made into a fine paste with the nitrite and then poured into hydrochloric acid.

As a rule the diazotisation proceeds best at a temperature of about 50° F. so that, except in hot weather, the use of ice for cooling is unnecessary.

Exceptions are Fast red bases G.L. and R.L., Fast scarlet G.G.S. base, Fast garnet G.C. base, Fast violet B. base, and the Fast blue bases B., R.R., and B.B., all of which diazotise best at about 60° F.

The diazo solutions and the developing liquors and printing colours made from them retain their stability best in the presence of free mineral acid; hence it is not advisable to neutralise their mineral acid content until immediately before use.

The Fast Colour Salts.—The Fast Colour Salts consist of the stabilised diazo salts of the bases. They come into the market in the form of dry, easily soluble powders and, being immediately available for use without tedious preparation, their employment in place of the corresponding bases is a great practical convenience and very much simplifies the methods of making-up developing solutions and printing colours. If stored in cool, dry rooms and protected from heat and light, they remain in good condition for a considerable time. The Fast Salts of the bases tabulated correspond for the most part to 20 per cent. of the base from which they are prepared, *i.e.* 100 parts of Fast Colour Salt are equivalent to 20 parts of base, but the following are exceptions: Fast Scarlet Salt G.G.S., 25 per cent.; Fast Scarlet Salt R., 25 per cent.; Fast Red Salt 3 G.L., 40 per cent.; Fast Blue Salt B.B., 40 per cent.; Fast Blue Salt R.R., 40 per cent.; Variamine Blue B. Salt, 50 per cent.

The diazo solutions are prepared simply by mixing the Fast Colour Salts quickly into a paste with about five times their weight of warm water at 75°-85° F., then adding cold water and, when solution is complete, making up to the required volume. Care must be taken not to allow the Fast Colour Salts to remain too long in contact with hot water before adding cold water; they are very stable at ordinary temperatures, but are decomposed by the prolonged influence of heat and must, therefore, be cooled as soon as possible after the initial pasting-up with warm water.

The Fast Colour Salts contain no free mineral acid and consequently require no neutralising with sodium acetate, etc., before use, except in the case of Fast Blue Salt B. (dianisidine), which requires an addition of sodium bicarbonate equal in weight to the colour salt used. A few other bases and colour salts require an addition of acetic acid to ensure their full development on strong prepares.

Direct Printing of Naphthol A.S. Colours.

The printing of Naphthol A.S. colours is carried out by exactly the same methods as those employed for β-naphthol colours, viz.:

(A.) By printing a pattern in a thickened solution of a naphthol followed by development in a diazo solution.

(B.) A modification of (A.).—Printing or padding naphthol solutions containing nitrite of soda on plain cloth, followed by development by printing or padding acid solutions of *undiazotised* bases. Known as Naphthol-nitrite Process.

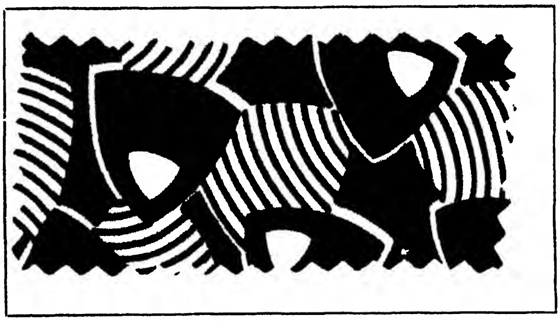
(C.) By printing thickened diazo solutions on naphthol-prepared cloth.

(A.) **The Printing of Thickened Naphthol A.S. Solutions followed by Development in Diazo Solutions.**—This process is particularly suitable for the printing of patterns consisting of widely spaced detached objects on a plain white ground—a type of pattern for which it is uneconomical to impregnate the whole body of the fabric with naphthol solution. It allows further of multi-colour patterns being produced from a *single* diazotised base, a feature which,

considering the instability of diazo compounds in general, constitutes a practical advantage of no mean order. For example, in the case of a six-colour pattern printed with naphtholates, there is only *one* diazo solution to prepare (in quantity just about sufficient for the work in hand), whereas if the same pattern were printed by the ordinary process (C.) the six different printing colours required would be made-up from six more or less unstable diazo solutions, and of each a goodly portion would be left unused, and useless, after the printing was completed.

Various other types of colouring matters, not susceptible to alkali and capable of being fixed by a short steaming, may be printed along with thickened Naphthol A.S. solutions, *e.g.* Basic colours, Chrome colours, and Vat and Sulphur colours. Aniline black and similar oxidation colours are not suitable for direct printing. On the other hand, however, the naphthol printing process provides a valuable means for obtaining Azoic colour resist effects under slop-padded Aniline black grounds. Examples and description of this style will be given later.

The composition of the Naphthol A.S. printing colours and the method of working the process are illustrated by the two following examples:—



(I.G.)

Red: Naphthol A.S.-D. } developed with Fast Scarlet
Brown: Naphthol A.S.-L.B. } G. base.

NAPHTHOL PRINTING COLOURS.

	Scarlet.	Brown.
Naphthol A.S.-D.	20 grms.	..
Naphthol A.S.-L.B.	..	20 grms.
Oleine or Monopol Brilliant Oil .	30 ,,	30 ,,
Caustic soda 72° Tw.	20 ,,	30 ,,
Methylated spirit	50 ,,	50 ,,
Glyecine A.	..	50 ,,
Water	380 ,,	320 ,,
Dissolve and mix with—		
Tragacanth thickening 60/1000 .	500 ,,	500 ,,
	1000 grms.	

Print, dry, and develop, in a padding mangle, in the following diazo solution.

DEVELOPING SOLUTION.

13·3	grms.	Fast Scarlet base G.
26·6	c.c.	hydrochloric acid 33° Tw.
130	,,	boiling water.
Dissolve, cool, and add—		
200	,,	ice water.

When cooled to about 50° F. add slowly—

6·7	grms.	nitrite of soda.
25	c.c.	water.

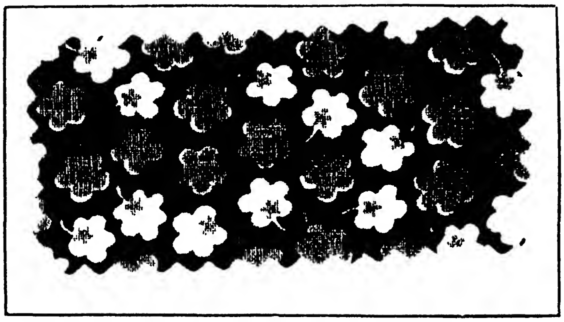
Allow to stand 10–15 minutes, then add—

14	grms.	acetate of soda.
50	c.c.	water.

Make up with water to 1000 c.c.

After development in the padding mangle the goods are given an air passage of about 1 minute, then passed at 200°–212° F. through a bath containing 20 c.c. of sodium bisulphite 71° Tw. per litre, and finally washed, soaped at the boil, washed again, and dried. The developing, airing, and washing are carried out on the machine illustrated in fig. 81 ; the soaping and last washing may be done in the rope form.

The pattern below, in red and pink, has been produced in a similar manner.



Naphthol A.S.-R.L., developed in Fast Red R.L. base (I.G.).

Printing Colour.

	Red.	Pink.
Naphthol A.S.-R.L.	10 grms.	1 grm.
Monopol Brilliant Oil	10 ,,	10 grms.
Caustic soda 70° Tw.	20 ,,	10 ,,
Water	460 ,,	479 ,,
Neutral starch-tragacanth paste	500 ,,	500 ,,
	1000 grms.	

Developing Solution.

7	grms.	Fast Red R.L. base.
15	c.c.	hot water.

Make into a smooth paste and add—

3·5 grms. sodium nitrite.

When the nitrite is dissolved, stir in small portions into—

200	c.c.	cold water.
14	,,	hydrochloric acid 32° Tw.

Allow to stand ½ hour, stirring frequently ; then neutralise with—

7	grms.	acetate of soda.
20	c.c.	cold water.

Make up with water to 1000 c.c.

Print the Naphthol A.S.-R.L. red and pink on unprepared cloth, dry, develop as before in the foregoing solution, wash, soap, and wash.

By varying the naphthols and bases (or Fast Colour Salts) many multi-colour combinations of Azoic colours may be obtained, as may be gathered from the following table:—

Printing Naphthols.	Developer.	Colours Obtained.
A.S.-G. A.S.-B.S. A.S.-D. A.S.-T.R. A.S.-R.L. A.S.-B.O.	Fast Scarlet R.C. base.	Yellow. Pink. Scarlet. Red. Dull orange. Claret.
A.S.-G. A.S.-D. A.S.-T.R. A.S.-B.O.	Fast Scarlet T.R. base.	Yellow. Orange. Scarlet. Bordeaux.
A.S.-G. A.S. A.S.-B.G.	Fast Scarlet Salt G.G.S.	Yellow. Scarlet. Brown.
A.S.-G. A.S.-R.L. (weak) A.S.-R.L. A.S.-D.	Fast Red R.L. base.	Orange. Pink. Red. Bordeaux.
A.S.-G. A.S. A.S.-B.G.	Fast Violet B. base.	Brownish-yellow. Violet. Bordeaux.
A.S.-G. A.S.	Fast Blue R.R. base.	Brownish-orange. Blue.

All the A.S. Naphthols may be thickened and printed in the manner just described; and all the bases and Fast Colour Salts may be used for developing, with the exception of Fast Blue B. base, Fast Black B. base, and Fast Garnet G.C. and G.B.C. bases, which stain the white background more or less strongly and permanently.

If Basic, Chrome, or Vat colours are printed along with thickened naphthols, the goods, after printing and before developing, are steamed for 4–6 minutes in the rapid ager. Thereafter the process proceeds as just described. When Basic colours are used, 5 grms. of tartar-emetic are added to each litre of the developing bath and Glyecine A. or Fibrit D. is used in place of organic acids for dissolving the dyestuff in the printing colour. Such mixed colourings find but little employment in the printed naphthol process, being more conveniently and reliably produced by other means.

(B.) **The Naphthol-Nitrite Process.**—The characteristic feature of the naphthol-nitrite method for the production of Azoic colours is that the diazotisation of the base and its coupling with an appropriate naphthol of the A.S. series are both effected, simultaneously, on the fibre.

The process may be worked in two ways:

(*a*) By printing, on unprepared cloth, one or several Naphthol A.S. solutions containing nitrite of soda, followed by development in an acid

solution of a salt of an undiazotised base. This is known as the Naphthol-Nitrite Printing Process.

(*b*) By padding bleached cloth with a Naphthol A.S. solution containing nitrite of soda, followed by printing one or more thickened acid solutions of salts of undiazotised bases. Known as the Naphthol-Nitrite Padding Process.

The difference between (*a*) and (*b*) is that in (*a*) only *one base* but several naphthols may be used, whereas in (*b*) the reverse is the case, only *one naphthol* but several bases being possible.

As soon as the padded or printed solutions of the bases come in contact with the naphthol-nitrite mixtures already on the cloth, their acid content decomposes the nitrite, liberating nitrous acid which, at once, diazotises the base, and the diazo compound thus formed couples immediately with the naphthols.

The process is adapted only to bases whose hydrochlorides are soluble in water. These hydrochlorides themselves are sufficiently acid to bring about diazotisation and coupling with the naphthol; but their effect is accelerated by additions of organic acids, such as glycollic acid and lactic acid, both of which hasten the coupling considerably.

(a) *The Naphthol-Nitrite Printing Process.*—This process is particularly suited to the printing of small patterns on a white ground, especially in cases where the naphthol-nitrite prepare of the alternative process (see (*b*)) exerts an injurious effect on colours of other classes which may be required to work along with the naphthol-nitrite printing colours. Colours of the Basic, Chrome, and Vat colour groups, which can be fixed by a short steaming, may be used safely in combination with naphthol-nitrite printing pastes; Aniline and Logwood blacks, and most vegetable dyestuffs, are inadmissible on account of their sensitiveness to acids and alkalies.

The following examples will suffice to illustrate the application of the naphthol-nitrite process of printing Azoic colours:—

NAPHTHOL-NITRITE PRINTING COLOURS.

	Yellow.	Red.
Naphthol A.S.-G.	25 grms.	..
Naphthol A.S.-D.	..	25 grms.
Oleine 40 per cent.	30 „	30 „
Caustic soda 62° Tw.	40 „	40 „
Mix to a smooth paste and dissolve in—		
Boiling water	245 „	245 „
Then add—		
Neutral starch-tragacanth paste	570 „	570 „
Sodium nitrite solution 1 : 2	90 „	90 „
	1000 grms.	

DEVELOPING SOLUTION.

15 grms. Fast Red K.B. base.
50 „ glycollic acid.
950 c.c. hot water.

Dissolve, cool, and make up to—

1000 c.c.

A typical Basic colour for printing with the above red and yellow is prepared as follows :—

Light Blue Printing Colour.

$$\left\{\begin{array}{rll} 40 & \text{grms.} & \text{Victoria blue B.A.} \\ 60 & ,, & \text{Glycecine A. or Fibrit D.} \\ 300 & ,, & \text{water.} \end{array}\right.$$

Dissolve and add—

250	grms.	starch-tragacanth paste.
150	,,	British gum solution 1 : 1.
200	,,	tannin-alcohol 1 : 1.
1000		

When this blue or other Basic colours form part of the colour combination, the developing bath requires an addition of 5 grms. of tartar-emetic per litre ; Chrome and Vat colours require no addition.

Unprepared bleached cloth is printed with the foregoing naphthol-nitrite red and yellow, dried and, if the pattern contains supplementary colours which require steaming, given a 4–6 minutes' passage through a rapid ager. It is then developed in a padding machine through the acidified solution of Fast Red K.B. base, allowed to run in air for a short time to complete the coupling and, finally, passed in the open width through a beck of boiling water, washed, soaped, and dried. When the supplementary colours include Vat or Sulphur dyestuffs, an oxidising bath of bichromate or perborate of soda is introduced before the first wash.

The two preceding general methods of printing thickened naphthol and naphthol-nitrite solutions present no practical difficulties ; they yield clean, sharp impressions of the pattern and the white grounds remain unstained ; any Naphthol A.S. may be used, including Naphthol A.S.-B.R., which is too strongly substantive to employ in any other printing process ; and practically any base soluble in hydrochloric acid may be used for coupling except, as before mentioned, the Blue, Black, and Garnet bases, which stain the white ground.

(b) *The Naphthol-Nitrite Padding Process.*—In this modification of the naphthol-nitrite process the entire fabric is first prepared by padding in a solution of Naphthol A.S., etc., containing the requisite amount of nitrite of soda, being afterwards printed with the soluble acid salts of various amino-bases. As in process (*a*) the diazotisation and coupling proceed simultaneously on the fibre, the Azoic colour being formed almost instantaneously.

The bases, being printed, only fall on the cloth within the limits of the pattern and, consequently, any acid-soluble base may be employed irrespective of the staining property it may possess when applied as a padded developing solution. Conversely, only such naphthols of the A.S. group are applicable as are readily removed from the cloth by washing and soaping ; Naphthols A.S.-B.R. and A.S.-G.R. are not suitable for the naphthol-nitrite padding process, though both may be used for the alternative printing process (*a*).

The diazotisation and coupling of the printed bases are hastened by additions of formic, oxalic, citric, lactic, tartaric, or glycollic acid, and also acid salts of the order of aluminium sulphate, bisulphate of soda, etc., to the printing colours.

Supplementary colours of other groups may be worked in combination with the printed bases, provided that only such are selected as are not in-

juriously affected by the nitrite in the prepare. Of these the most suitable will be found amongst the Chrome and Vat colours, though many Basic dyestuffs are also available. On the whole, mixed colourings of this description are preferably executed by other methods.

Satisfactory results are obtained by combinations of the following naphthols and bases:—

NAPHTHOLS FOR PREPARING.

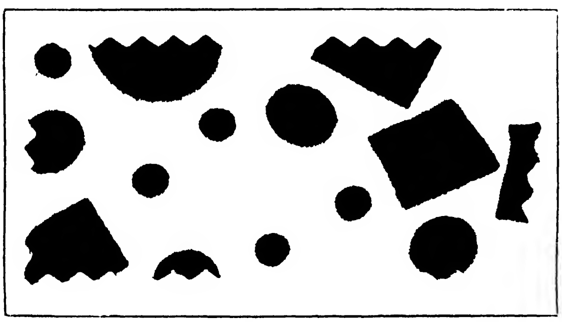
Naphthol A.S.-G.	Naphthol A.S.-B.G.
,, A.S.	,, A.S.-B.S.
,, A.S.-D.	,, A.S.-T.R.
,, A.S.-O.L.	,, A.S.-E.
,, A.S.-R.L.	,, A.S.-B.O.

BASES FOR PRINTING.

Fast Yellow G.C. base.	Fast Scarlet T.R. base.
,, Orange G.C. ,,	,, Red K.B. ,,
,, Scarlet G. ,,	,, ,, R.C. ,,
,, ,, G.G.S. ,,	,, ,, T.R. ,,
,, ,, R.C. ,,	,, Blue B. ,,

Fast Black B. base.

The method of working the naphthol-nitrite padding process, and the style of pattern adapted to its application, are illustrated by the example below:—



(I.G.)

Fast Red K.B. base. } printed on a prepare of Naphthol
Fast Black B. base. } A.S.-O.L. and nitrite.

Pad the cloth in the following liquor in a 3-bowl mangle:—

NAPHTHOL A.S.-O.L. PREPARE.

20 grms. Naphthol A.S.-O.L.
30 c.c. oleine or Monopol Brilliant Oil.
30 ,, caustic soda 62° Tw.
300 ,, hot water.

Boil, if necessary, to dissolve, and add—

25 grms. sodium nitrite.
2 ,, Nekal B.X. dry.

Make up to 1000 c.c.

The small addition of Nekal B.X. is optional, but it promotes better penetration of the naphthol.

Pad hot, dry, and run the cloth over a series of rollers to cool before winding-on for printing. Then print the following two colours :—

Printing Solution.	Red.	Black.
Fast Red K.B. base	15 grms.	..
Fast Black B. base	..	24 grms.
Tartaric acid solution 50 per cent.	75 ,,	75 ,,
Lactic acid 50 per cent.	75 ,,	75 ,,
Water	150 ,,	150 ,,
Dissolve and add—		
Neutral starch-tragacanth paste	500 ,,	500 ,,
Make up to	1000 grms.	

Cool down before printing.

After printing, soap at 180°–200° F. in

5 grms. soap.
0·5 ,, soda-ash.
1000 c.c. water.

Wash and dry.

A similar effect in orange and claret is obtained by preparing with Naphthol A.S.-T.R. and printing Fast Orange G.C. base and Fast Red R.C. base. Thus :—

Naphthol A.S.-T.R. Prepare.

20 grms. Naphthol A.S.-T.R.
10 c.c. methylated spirit (to wet-out).
30 ,, oleine.
20 ,, caustic soda 62° Tw.
500 ,, boiling water.

Dissolve and add—

25 grms. nitrite of soda.
2 ,, Nekal B.X.

Make up to 1000 c.c.

Printing Solution.

Orange : 15 grms. per kilo. Fast Orange G.C. base
Claret : 16 ,, ,, ,, Fast Red R.C. base

both made-up exactly as Fast Red K.B. base in pattern illustrated.

In like manner red and pink prints are produced by printing two strengths of Fast Red K.B. base on a prepare of 20 grms. Naphthol A.S.-D./25 grms. sodium nitrite per litre of preparing liquor.

Although the colour combinations obtainable from the two naphthol-nitrite processes are limited in range by the number of water-soluble bases available, the processes themselves possess two considerable advantages, (i) they avoid the use of unstable diazotised compounds in the printing colours and developing liquors, and (ii) they save a good deal of time in preparation and are economical in use, since the printing colours and developing liquors do not deteriorate on keeping. They also ensure a clean white ground without resort to special soaping and clearing, and, in styles containing no supplementary steam colours, they require no ageing, steaming, or fixing operations.

An attractive, simple, and fast style, which does not appear to have been worked as yet, might possibly be produced by printing Indigosols (nitrite

process) along with naphthol-nitrite printing colours on plain unprepared cloth. One might reasonably suppose that both Azoic colours and Indigosols would develop together during the passage through acidified solutions of the colour bases. Any trouble from the reserving action of alkali "scum" on the Indigosols could be counteracted by an addition of sulphate of ammonia to the Indigosol printing colours. In this way very fast combinations of Azoic and Vat colours might be obtained without the necessity for steaming or for a previous preparation of the cloth.

(C.)—**The Printing of Thickened Diazo Solutions on Cloth previously Prepared with Naphthol A.S.**—The working methods of this most popular and comprehensive process for the printing of Azoic colours are identical with those already discussed under the same caption in the description of "The β-Naphthol or Older Azoic Colours," and the remarks made there on the general conduct of the process apply equally well here. In a few instances the properties of some members of the Naphthol A.S. group, and of certain Fast Colour Bases, have necessitated slight modifications in the procedure of padding and in the preparation of printing colours, but apart from these minor variations in detail the processes remain the same.

The replacement of β-naphthol by Naphthol A.S. products has, however, added greatly to the possibilities of this method of printing Azoic colours—particularly so in the direction of enabling it to be applied to the production of many fast styles of work for which the older β-naphthol colours were totally unsuited. All the Fast Bases or Fast Colour Salts and all the new Naphthols (except Naphthols A.S.-B.R. and A.S.-G.R. which, owing to their strong affinity for the fibre, cannot be washed out completely) are available for printing purposes; and, as each base can be coupled with each naphthol, upwards of 400 colour combinations are possible, not taking into account lighter shades of each. Many of these colours are characterised by being extremely bright and of excellent all-round fastness; others, equally bright, may be classed as of very good fastness to all conditions; and the rest, for the most part, may be regarded as of good general fastness, superior in many respects to the ordinary fast steam colours. A few are deficient in some quality, lacking, perhaps, in resistance to light, soaping, or other destructive agency; these fall below the standard of fastness and are rarely used, being readily replaced by later additions not subject to these drawbacks. Although numerous combinations of different naphthols with various Fast Bases give many colours which resemble each other closely in shade and properties, they nevertheless comprise a well-graduated and nearly complete colour scale (only a green is missing) from which the textile colourist is able to select a range of colours suitable for almost any style and capable of fulfilling the conditions of any recognised standard of fastness.

One of the most important factors in the successful printing of diazo solutions on naphthol-prepared cloth is the observance of a proper relationship between the quantity of naphthol on the cloth and the concentration of diazo compound in the printing colour. A slight excess of naphthol does not matter so much, except that it represents waste, but an excess of diazotised base yields duller colours (especially on steaming) and, if not completely decomposed in drying after printing, is dissolved out during subsequent washing operations and stains the unprinted parts of the cloth by coupling with the naphthol still remaining there.

The following tabular survey of the relative proportions of the more important Naphthols and Fast Bases has been compiled from data supplied by the I. G. Farbenindustrie A.G. of Frankfurt, the manufacturers of Naphthol A.S. products.

(I.) Relative Proportions of Naphthol and Base in Preparing Liquors and Printing Colours (or Developing Solutions) respectively.

One part of the following Naphthols requires the tabulated parts of Bases:—

Bases:	Naphthols:												
	A.S.	A.S.-B.S.	A.S.-B.O.	A.S.-R.L.	A.S.-S.W.	A.S.-B.G.	A.S.-T.R.	A.S.-D.	A.S.-G.	A.S.-O.L.	A.S.-I.T.R.	A.S.-L.B.	A.S.-L.T.
Fast Yellow G.C. base	0·85	0·7	0·7	0·75	0·7	0·7	0·7	0·75	0·85	0·75	..	..	..
,, Orange G.C. base	0·85	0·7	0·7	0·75	0·7	0·7	0·7	0·75	0·85	0·75	..	0·3	..
,, ,, G.R. base	0·7	0·6	0·6	0·65	0·6	0·55	0·6	0·65	0·75	0·65	..	0·25	..
,, ,, R. base	0·7	0·6	0·6	0·65	0·6	0·55	0·6	0·65	0·75	0·65	..	..	..
,, ,, Salt R.D.	4·25	..	..	3·8	..	..	..	..	..	3·8	..	..	..
,, Scarlet G.G.S. base	1·15	1	1	1	1	0·9	1	1	1·2	1	..	..	..
,, ,, G. base	0·75	0·65	0·65	0·7	0·65	0·6	0·65	0·7	0·8	0·7	..	0·25	..
,, ,, R.C. base	1·15	1	1	1	1	0·9	1	1	1·2	1	..	..	..
,, ,, T.R. base	1	0·85	0·85	0·9	0·85	0·8	0·85	0·9	1·1	0·9	..	0·35	..
,, Red K.B. base	1	0·85	0·85	0·9	0·85	0·8	0·85	0·9	1·1	0·9	..	..	..
,, ,, T.R. base	1	0·85	0·85	0·9	0·85	0·8	0·85	0·9	1·1	0·9	..	..	0·7
,, ,, 3 G.L. base spec.	1·75	1·5	1·5	1·6	1·5	1·4	1·5	1·6	1·85	1·6	..	..	..
,, ,, G.L. base	0·75	0·65	0·65	0·7	0·65	0·6	0·65	0·7	0·8	0·7	..	..	..
,, ,, R.L. base	0·75	0·65	0·65	0·7	0·65	0·6	0·65	0·7	0·8	0·7	..	0·25	..
,, ,, R.C. base	1	0·85	0·85	0·9	0·85	0·8	0·85	0·9	1·1	0·9	..	0·35	..
,, ,, B. base	0·9	0·75	0·75	0·8	0·75	0·7	0·75	0·8	0·9	0·8	..	0·3	..
,, ,, I.T.R. base	..	..	..	..	..	..	..	..	..	..	0·9	..	..
,, Bordeaux G.P. base	0·9	0·75	0·75	0·8	0·75	0·7	0·75	0·8	0·9	0·8	..	..	..
,, Garnet G.C. base	1·4	1·2	1·2	1·3	1·2	1·2	1·2	1·3	1·5	1·3	..	..	..
,, ,, G.B.C. base	1·4	1·2	1·2	1·3	1·2	1·2	1·2	1·3	1·5	1·3	..	..	..
,, Violet B. base	1·1	1	1	1·1	1	1	1	1·1	1·1	1·1	..	..	..
,, Corinth L.B. base	1·2	..	..	1·2	..	..	..	..	..	..	..	..	1·28
,, ,, Salt V.	3·75	3·2	3·15	3·35	3·15	3·05	3·2	3·55	..	3·35	..	..	..
Variamine Blue B.	1·13	1·05	1·05	1·1	1·05	1·05	1·05	1·1	1·13	1·1	..	..	..
Fast Blue B. base	0·6	0·55	0·55	0·6	0·55	0·5	0·55	0·6	0·65	0·6	..	..	..
,, ,, R.R. base	1·15	1·1	1·1	1·15	1·1	1	1·1	1·15	1·15	1·15	..	..	..
,, ,, B.B. base	1·4	1·2	1·2	1·3	1·2	1·2	1·2	1·3	1·5	1·3	..	..	..

As a rather smaller proportion of base is usually taken for printing, the above quantities may be reduced by about 5 per cent. without detriment to the shades.

This table, used in conjunction with the following synopsis of "Diazotising Quantities of the Principal Fast Bases," will serve as a guide to the preparation of full-strength printing colours suitable for any given concentration of naphthol prepare.

(II.) DIAZOTISING QUANTITIES OF THE PRINCIPAL FAST BASES.

	100 grms. Base require:			
	Hydrochloric Acid 32° Tw.	Sodium Nitrite.	Sodium Acetate.	Ice.
Section (a).				
Fast Yellow G.C. base	120 c.c.	46 grms.	90 grms.	..
,, Orange G.C. base	120 ,,	46 ,,	90 ,,	..
,, Scarlet G.G.S. base	200 ,,	36 ,,	50 ,,	..
,, ,, G. base	200 ,,	50 ,,	100 ,,	..
,, ,, R.C. base	90 ,,	34 ,,	67 ,,	..
,, ,, T.R. base	100 ,,	40 ,,	75 ,,	..
,, Red K.B. base	100 ,,	40 ,,	75 ,,	..
,, ,, T.R. base	100 ,,	40 ,,	75 ,,	..
,, ,, I.T.R. base	105 ,,	30 ,,	67 ,,	..
,, ,, R.C. base	100 ,,	40 ,,	75 ,,	..
,, Garnet G.C. base	70 ,,	28 ,,	53 ,,	500 grms.
,, ,, G.B.C. base	70 ,,	28 ,,	53 ,,	500 ,,
,, Corinth L.B. base	117 ,,	67 ,,	45 ,,	..
,, Blue B. base	240 ,,	65 ,,	125 ,,	..
,, ,, B.B. base	100 ,,	25 ,,	45 ,,	..
,, ,, R.R. base	110 ,,	27·5 ,,	50 ,,	..
	Sodium Nitrite.	Hydrochloric Acid 32° Tw.	Sodium Acetate.	
Section (b).				
Fast Orange G.R. base	54 grms.	214 c.c.	110 grms.	..
,, ,, R. base	54 ,,	214 ,,	110 ,,	..
,, Red 3 G.L. special base	21·5 ,,	86 ,,	43 ,,	..
,, ,, G.L. base	50 ,,	200 ,,	100 ,,	..
,, ,, R.L. base	50 ,,	200 ,,	100 ,,	..
,, ,, B. base	43 ,,	170 ,,	85 ,,	..
,, Bordeaux G.P. base	43 ,,	170 ,,	85 ,,	..
,, Violet B. base	30 ,,	115 ,,	60 ,,	..

Variamine Blue B. is diazotised by a special method; only the corresponding Fast Blue Salt is now available.

The bases are diazotised in different ways according to their solubility in dilute hydrochloric acid, thus:

SECTION (*a*): SOLUBLE BASES—EXAMPLE.

$\left\{\begin{array}{ll}\text{100 grms.} & \text{Fast Orange G.C. base.}\\ \text{500 c.c.} & \text{hot water.}\\ \text{120 ,,} & \text{hydrochloric acid 32° Tw.}\end{array}\right.$

Mix to a fine paste and dissolve by adding—

1500 c.c. cold water.

Cool to 40° F. with ice (if necessary) and add—

46 grms. nitrite of soda.
200 c.c. cold water.

Allow to react for about ½ hour; then neutralise with—

90 grms. acetate of soda.
300 c.c. water.

Make up to required volume with water or thickening.

SECTION (*b*): INSOLUBLE OR DIFFICULTLY SOLUBLE BASES—EXAMPLE.

100 grms. Fast Red 3 G.L. base special.
200 c.c. hot water.
21·5 grms. nitrite of soda.

Work into a fine paste and when the nitrite is dissolved cool down and stir in small portions into—

1000 c.c. ice water.
86 „ hydrochloric acid 32° Tw.

Stir repeatedly for ½ hour, filter, and add—

43 grms. acetate of soda.
200 c.c. cold water.

Make up to required volume with water or thickening.

Note.—When diazotising Fast Orange bases G.R. and R., the paste of base and nitrite of soda is stirred *quickly* into the dilute hydrochloric acid—not in small portions—to avoid formation of diazo-amino compounds.

The method of using the two foregoing tables (I. and II.) as an aid in calculating the quantity of any Fast Base required in a printing colour or dye liquor to correspond to a given concentration of a prepare of any Naphthol of the A.S. series, is illustrated by the following example.

Example.—

Fast Red T.R. base is to be printed on a prepare of Naphthol A.S.-D., 20 grms. per litre.

Reference to table of relative proportions (I.) shows that

1 part Naphthol A.S.-D. = 0·9 part Fast Red T.R. base.
∴ 20 parts „ „ = 18 parts „ „ „

As rather less base is usually taken for printing than for developing, 17 grms. Fast Red T.R. base per kilo. of printing colour will be sufficient for 20 grms./litre Naphthol A.S.-D. prepare.

For calculating the full recipe for a printing colour of this concentration the given figures for Fast Red T.R. base in the table of diazotising quantities (II.) are multiplied by 0·17, thus giving, with water and thickening, the following recipe:—

17	grms.	Fast Red T.R. base.
17	c.c.	hydrochloric acid 32° Tw.
340	„	cold water.
6·8	grms.	sodium nitrite.
35	c.c.	water.
12·75	grms.	sodium acetate.
50	c.c.	water.
Add—		
500	grms.	neutral starch-tragacanth paste.
Make up to 1000	grms.	

If Fast Red Salt T.R. is used in place of the base the recipe is simplified, the salt already being diazotised. It represents 20 per cent. of the base.

{ 85	grms.	Fast Red Salt T.R.
{ 415	,,	water.
500	,,	neutral starch-tragacanth paste.
1000		

The figures for other Bases and Fast Colour Salts and various Naphthols are obtained in exactly the same way. Light shades are, of course, obtained simply by adding extra starch-tragacanth paste as required, together with a little acetic acid.

Addition of Acetic Acid to Printing Colours.—In certain cases the addition of acetic acid to printing colours enhances the brilliancy of the shades. This effect is particularly noticeable in prints produced with various diazo solutions on a grounding of Naphthol A.S.-G., the yellows so obtained being much purer and clearer than those printed without acetic acid. Similar beneficial results accrue from the addition of acetic acid to printing colours made-up from the following bases or their corresponding Fast Colour Salts:—

Fast Yellow G.C. base.	Fast Red 3 G.L. base.
,, Orange G.C. base.	,, Violet B. base.
,, ,, G.R. base.	Variamine Blue B. base.

The usual addition is 20–30 grms. acetic acid, 50 per cent., per litre of printing colour; it is more or less optional for very dark shades, but of great advantage for light and medium colours.

When dark and light shades are printed together on a strong naphthol prepare, *e.g.* red and pink, dark and light blues, black and violet, etc., it is essential to add acetic acid to the *light* colours in order to neutralise the excess of alkali in the prepare. Light colours reduced from dark ones by addition of thickening have their acidity reduced along with their shade and, consequently, would not couple with the naphthol if the deficiency were not made good by addition of extra acid. In any case it is not advisable to attempt to print very light shades of Azoic colours; weak diazo solutions are very unstable and couple slowly.

In the case of Fast Black Salt K. it is *absolutely essential* to add a considerable amount of acetic acid to the printing colour, otherwise it is impossible to obtain a full rich black. A shortage of acid yields dark violet-blues of little interest; but two-colour prints of a full black and a weaker shade of it (plus acetic acid) give a not unpleasant black and violet effect.

Printing and After-treatment of Goods.—The actual printing and finishing-off of the goods call for little comment as they are carried out in exactly the same manner as for β-naphthol colours, viz. the cloth is first impregnated with a Naphthol A.S. solution, dried in a hot-flue and then printed with thickened diazo solutions, after which it is washed, soaped at the boil, washed again. and finally dried. The printed pieces may be stored safely for several days before being washed off, provided that they are protected from light, moisture, and acid fumes.

The pieces to be printed are padded, in a 3-bowl mangle giving two immersions, with a solution of a naphthol of the A.S. group appropriate to the shade desired. The general composition of the padding solutions or "prepares" is indicated in the following table:—

NAPHTHOL A.S. "PREPARES."

Naphthol.		Caustic Soda 62° Tw.	Oleine.	Nekal B.X. Dry.
A.S.-G.	15 grms.	22·5 c.c.	20 c.c.	2 grms.
A.S.	15 ,,	22·5 ,,	20 ,,	2 ,,
A.S.-D.	15 ,,	22·5 ,,	20 ,,	2 ,,
A.S.-O.L.	15 ,,	22·5 ,,	20 ,,	2 ,,
A.S.-R.L.	15 ,,	30·0 ,,	20 ,,	2 ,,
A.S.-B.G.	15 ,,	30·0 ,,	20 ,,	2 ,,
A.S.-B.S.	15 ,,	22·5 ,,	20 ,,	2 ,,
A.S.-T.R.	15 ,,	30·0 ,,	20 ,,	2 ,,
A.S.-I.T.R.	13 ,,	22·5 ,,	20 ,,	2 ,,
A.S.-L.T.	14 ,,	28 ,,	20 ,,	2 ,,
A.S.-E.	15 ,,	30 ,,	20 ,,	2 ,,
A.S.-L.B.	20 ,,	16 ,,	20 ,,	2 ,,
A.S.-B.O.	15 ,,	30 ,,	20 ,,	2 ,,
A.S.-S.W.	15 ,,	30 ,,	20 ,,	2 ,,
Made up to 1000 c.c.				

The addition of Nekal B.X. dry promotes better penetration of the diazo compound during the subsequent printing and, consequently, a better and fuller impression of the more finely engraved parts of a pattern.

Pale shades of pink, blue, violet, etc., may be printed on weaker prepares if no dark colours occur along with them ; but in such cases the caustic soda and oleine ought not to be reduced below 10 c.c. and 20 c.c. per litre, respectively.

With the more highly substantive naphthols—from Naphthol A.S.-T.R. downwards in the above list—it is advisable to commence the padding with a somewhat weaker solution of naphthol and to replenish the padding-box with full-strength liquor as the padding proceeds, keeping the level of the liquor in the box as constant as possible. The degree of dilution of the starting bath cannot be stated definitely ; it varies with the speed of the mangle, the temperature of padding, the duration of the immersion of the cloth and the substantivity of the naphthol in use. A usual dilution is 3 : 1 (3 parts strong solution, 1 part water), but sometimes 5 : 1 is little enough and in other cases 2 : 1 is not too much for such naphthols as A.S.-B.O. and A.S.-S.W. ; the quicker the rate of padding and the higher the temperature, the less the dilution required. The effect of substantivity can best be neutralised by padding the goods quickly at a temperature not lower than 160° F. ; the immersion is short and the high temperature reduces the affinity of the naphthols for the fibre to a point at which it is negligible.

The padded goods are dried rapidly in a hot-flue at 170°–175° F., or over cylinders, and then printed with the required diazo solutions of Fast Bases or with their Fast Colour Salts.

Of the numerous combinations possible, those most in vogue for direct printing are detailed in the following list together with the quantities of naphthol per litre of "prepare" and of base per kilo. of printing colour. They furnish graduated ranges of every colour except green, and may be reduced as required to give light shades of pink, violet, blue, salmon, fawn, etc., on the same naphthol grounding.

For Red.

15 grms. Naphthol A.S.	16 grms. Fast Scarlet R.C. base.
* 17 ,, ,, ,,	70 ,, ,, Red Salt 3 G.L.
20 ,, ,, A.S.-D.	17 ,, ,, ,, K.B. base.
15 ,, ,, ,,	9 ,, ,, Orange G.R. base.
15 ,, ,, A.S.-T.R.	12 ,, ,, Red T.R. base.
* 15 ,, ,, A.S.-R.L.	10 ,, ,, ,, R.L. base.
15 ,, ,, A.S.-O.L.	13 ,, ,, ,, R.C. base.
13 ,, ,, A.S.-I.T.R.	16 ,, ,, ,, I.T.R. base.
14 ,, ,, A.S.-L.T.	10 ,, ,, ,, T.R. base.

For Scarlet.

15 grms. Naphthol A.S.-O.L.	10 grms. Fast Scarlet G. base.
15 ,, ,, A.S.	65 ,, ,, ,, Salt G.G.S.
15 ,, ,, A.S.-D.	10 ,, ,, ,, G. base.
15 ,, ,, A.S.-T.R.	12 ,, ,, ,, T.R. base.

For Orange.

15 grms. Naphthol A.S.-D.	10 grms. Fast Orange G.C. base.
15 ,, ,, A.S.-O.L.	10 ,, ,, ,, ,, ,,
15 ,, ,, A.S.	10 ,, ,, ,, G.R. base.
* 15 ,, ,, A.S.	50 ,, ,, ,, Salt R.D.
* 15 ,, ,, A.S.-R.L.	50 ,, ,, ,, ,, ,,

For Yellow.

15 grms. Naphthol A.S.-G.	12 grms. Fast Yellow G.C. base.
15 ,, ,, ,,	15 ,, ,, Red K.B. base.
15 ,, ,, ,,	70 ,, ,, Scarlet Salt G.G.S.
15 ,, ,, ,,	15 ,, ,, ,, T.R. base.

For Blue.

15 grms. Naphthol A.S.	34 grms. Variamine Blue Salt B.
12 ,, ,, ,,	16 ,, Fast Blue B.B. base.
12 ,, ,, ,,	13 ,, ,, ,, R.R. base.
8 ,, ,, ,,	4 ,, ,, ,, B. base.
8 ,, ,, A.S.-T.R.	4 ,, ,, ,, ,, ,,
8 ,, ,, A.S.-D.	4 ,, ,, ,, ,, ,,

For Violet.

4 grms. Naphthol A.S.	20 grms. Fast Violet Salt B.
4 ,, ,, A.S.-T.R.	20 ,, ,, ,, ,,

For Bordeaux.

20 grms. Naphthol A.S.-D.	17 grms. Fast Red T.R. base.
20 ,, ,, ,,	13 ,, ,, ,, R.L. ,,
* 12 ,, ,, A.S.-R.L.	9 ,, ,, ,, B. base.
* 15 ,, ,, A.S.-B.O.	11 ,, ,, ,, ,, ,,

For Claret.

20 grms. Naphthol A.S.-T.R.	22 grms. Fast Garnet G.B.C. base.
20 ,, ,, ,,	14 ,, ,, Bordeaux G.P. base.
15 ,, ,, A.S.-B.O.	11 ,, ,, ,, ,, ,,

For Corinth.

12 grms. Naphthol A.S.-D.	40 grms. Fast Corinth Salt V. conc.
14 ,, ,, A.S.-L.T.	18 ,, ,, ,, L.B. base.

FOR BROWN.

12 grms. Naphthol A.S.-B.G.	40 grms. Fast Scarlet Salt G.G.S.
20 ,, ,, A.S.-L.B.	10 ,, ,, ,, G. base.
20 ,, ,, ,,	40 ,, ,, Red Salt R.C.
20 ,, ,, ,,	40 ,, ,, Orange Salt G.C.

FOR BLACK.

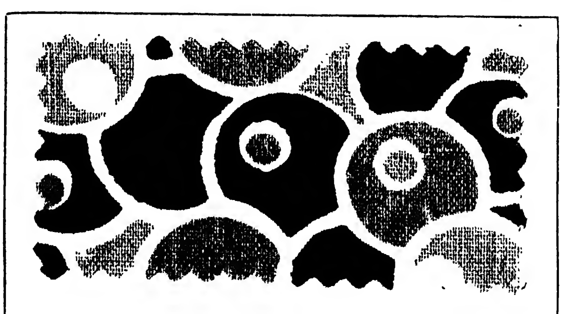
20 grms. Naphthol A.S.-D.	60 grms. Fast Black Salt K.
20 ,, ,, A.S.-R.L.	60 ,, ,, ,, ,, ,,

The combinations marked * are of exceptional all-round fastness.

After printing, the goods are first passed through a hot soda bath (2 grms. soda-ash per litre), then washed and soaped at the boil. The soda bath may be, and often is, replaced by a hot water wash; the soda facilitates, however, the removal of superfluous naphthol from the unprinted parts of the cloth and has a beneficial effect on the brightness of the finished print and is, therefore, to be recommended except when supplementary Basic and certain Chrome colours are printed along with Azoic colours.

For a purely Azoic colour print the hot soaping treatment is a very essential operation. It not only removes excess of colour and thickening material but, in most cases, it actually increases the fastness of the print to light and chlorine and, by modifying the physical state of the pigmentary colour molecules, enables and causes the dyestuff to penetrate more deeply into the body of the fabric and thus increases, also, fastness to rubbing. A *boiling* soap treatment is imperative for the full development of the true shades of Fast Violet B. base, the brown combination of Naphthol A.S.-B.G./Fast Scarlet Salt G.G.S., the pink shades of Naphthol A.S.-R.L./Fast Red R.L. base, and for numerous other combinations. As a general rule a hot soaping, at or near the boil, acts favourably on the development and increases the fastness and brilliancy of all Azoic colours of the better sort; it is, in short, an important factor in getting the best out of a range of splendid colours which, in addition to direct printed styles, lend themselves to a variety of applications greater, perhaps, than is obtainable from any other single group of dyestuffs.

The printed patterns in the following pages make no pretence to illustrate adequately, in point of numbers, the hundreds of colour combinations producible from various Fast Bases and Naphthols of the A.S. group. But they do provide examples of all the more important styles of printing, both old and new, to which these products are applicable; and it is hoped that they will suffice, together with the working details accompanying each, to give a fair idea of the wide field of usefulness covered by the Naphthol A.S. colours.



Diazo solutions printed on Naphthol A.S.-D. (I.G.).

Prepare.

Naphthol A.S.-D. 15 grms./litre (see " Naphthol Prepares ").

Printing Colours.

Orange.

50	grms.	Fast Orange Salt G.C.
30	,,	acetic acid 50 per cent.
420	,,	water 80° F.
500	,,	starch-tragacanth paste.
1000		

Black.

60	grms.	Fast Black Salt K.
90	,,	acetic acid 50 per cent.
350	,,	water 80° F.
500	,,	starch-tragacanth paste.
1000		

Red.

12	grms.	Fast Red K.B. base.
200	,,	water.
12	c.c.	hydrochloric acid 33° Tw.
5	grms.	sodium nitrite.
25	,,	water.
500	,,	starch-tragacanth paste.
20	,,	sodium acetate 1 : 1.
To 1000 grms.		

Pink.

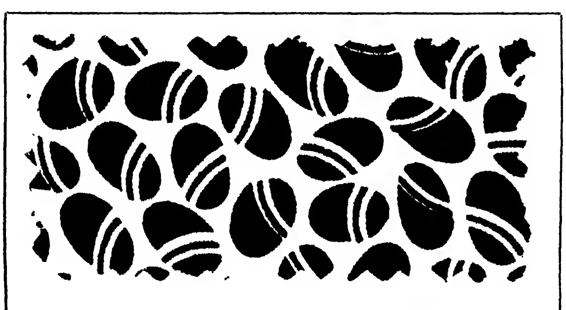
10	grms.	Fast Scarlet G. base.
100	,,	hot water.
20	c.c.	hydrochloric acid 33° Tw.
100	grms.	ice water.
5	,,	sodium nitrite.
25	,,	water.
500	,,	starch-tragacanth paste.
20	,,	acetate of soda 1 : 1.
To 1000 grms.		

For printing:

400	grms.	thickening.
100	,,	above pink.
10	c.c.	acetic acid 50 per cent.

The prepared and dried cloth is printed with the above four colours, dried, passed through a hot soda bath (2 grms./litre), washed, soaped at the boil, washed, and dried.

The next pattern represents a new version of a popular old style red and blue print. Its interest lies in the fastness of the blue: it is better to light and washing than Indigo and though not quite so fast as some of the vat colour blues, it is cheaper and easier to produce.



Fast Scarlet G. base and Variamine Blue Salt B. on Naphthol A.S. (I.G.).

PREPARE.

Naphthol A.S. 15 grms./litre.

PRINTING COLOURS.

Red.

11	grms.	Fast Scarlet G. base.
100	c.c.	water.
22	,,	hydrochloric acid 62° Tw.
100	,,	ice water.
5·5	grms.	sodium nitrite.
25	c.c.	water.
500	grms.	neutral starch-tragacanth paste.
20	,,	sodium acetate 1 : 1.

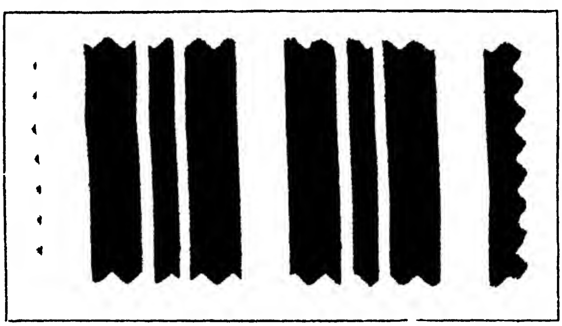
To 1000 grms.

Blue.

15	grms.	Variamine Blue Salt B.
20	,,	acetic acid 50 per cent.
465	,,	water.
500	,,	starch-tragacanth paste.
1000		

Prepare, dry, print, wash, etc., as preceding pattern.

Fast Violet B. base and its corresponding Fast Colour Salt yield shades of dark purple to bright violet which are unique amongst Azoic colours: there is not even a competitor of the same class.



Fast Violet B. base on Naphthol A.S. (I.G.).

PREPARE.

8 grms. Naphthol A.S. per litre (see " Naphthol Prepares ").

PRINTING COLOURS.

Dark Violet.

8	grms.	Fast Violet B. base.
40	,,	hot water.
2·4	,,	sodium nitrite.
200	,,	cold water.
9·2	c.c.	hydrochloric acid 33° Tw.
500	grms.	starch-tragacanth paste.
9	,,	sodium acetate 1 : 1.

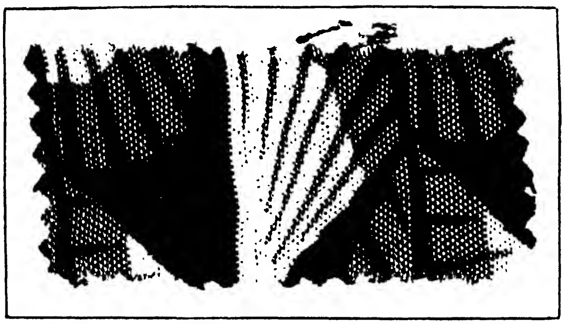
To 1000 grms.

Light Violet.

350	grms.	Dark violet (above).
295	,,	water.
325	,,	starch-tragacanth paste.
30	,,	acetic acid 50 per cent.
1000		

Prepare, print, etc., as before.

Although the most important use of Variamine Blue is as a ground for resist and discharge styles, it is also employed extensively as a printing colour in such styles as that shown in the following pattern. It is not a match for Indigo which it has, nevertheless, largely replaced, but it is a faster colour, and can readily be printed on fabrics, as illustrated here, which are unsuitable for printing with Indigo. Compared with vat colours of similar shade and depth it is cheaper; in the form of its Fast Colour Salt it is simpler to apply; and being also of good all-round fastness it finds considerable use in the production of high-class prints.



Variamine Blue Salt B. and Fast Black Salt K. on Naphthol A.S. (I.G.).
(Cotton and Viscose rayon fabric).

PREPARE.

Naphthol A.S., 15 grms./litre.

PRINTING COLOURS.

Blues.	Dark.	Light.
Variamine Blue Salt B.	15 grms.	2 grms.
Acetic acid 50 per cent.	20 ,,	20 ,,
Water	465 ,,	478 ,,
Starch-tragacanth paste	500 ,,	500 ,,
	1000 grms.	

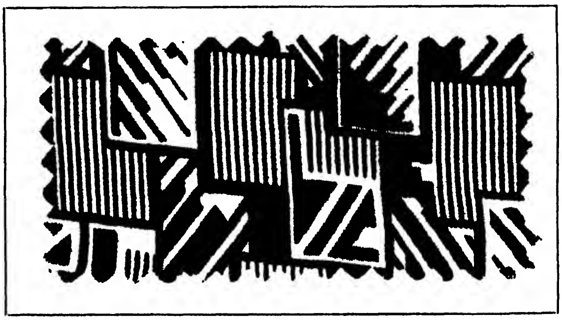
Black.

60	grms.	Fast Black Salt K.
90	,,	acetic acid 50 per cent.
350	,,	water.
500	,,	starch-tragacanth paste.
1000		

Prepare, dry, print, dry, pass through hot soda, etc., as already described.

Variamine Blue B. base is rarely used as such, owing to difficulties in diazotisation and coupling ; it has been replaced by its stable diazo compound, Variamine Blue Salt B.

Two later additions to the blue bases are Fast Blue B.B. base and Fast Blue R.R. base and their corresponding stable diazo salts, Fast Blue Salts B.B. and R.R. Fast Blue B.B. base produces bright blues, greener in tone than those of Variamine Blue B., whereas the R.R. base yields redder shades than either. Both the newer bases are suitable for the production of dark and light blues in direct printing on prepares of most Naphthols of the A.S. group, and are also used largely in resist and discharge printing. Although slightly inferior to Variamine Blue in fastness to light they are, on the contrary, much faster to chlorine—a great advantage from a printer's point of view, since it permits of the white grounds of prints being " cleared " in bleaching powder solution without injury to the colours.



Fast Blue Salt B.B. on Naphthol A.S. (I.G.).

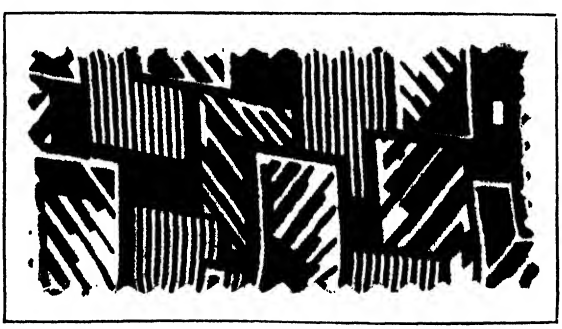
PREPARE.

Naphthol A.S., 15 grms./litre.

PRINTING COLOURS.

	Dark.	Light.
Fast Blue Salt B.B.	30 grms.	6 grms.
Acetic acid 50 per cent.	10 ,,	20 ,,
Water	460 ,,	474 ,,
Starch-tragacanth paste	500 ,,	500 ,,
	1000 grms.	

The pattern of Fast Blue Salt R.R. is produced according to the same formulæ.



Fast Blue Salt R.R. on Naphthol A.S. (I.G.).

If the bases are preferred for printing, on economic grounds, the following recipes may be used :—

Printing Colours.

	B.B.	R.R.
Fast Blue B.B. base	16 grms.	..
,, ,, R.R. base	..	13 grms.
Water	300 ,,	200 ,,
Hydrochloric acid 32° Tw.	16 c.c.	14·3 c.c.
Dissolve, cool, and add—		
Sodium nitrite	4 grms.	3·6 grms.
Water	40 ,,	30 ,,
Allow to stand 15 minutes then add—		
Starch-tragacanth paste	500 ,,	500 ,,
Sodium acetate	7·2 ,,	7·5 ,,
Water	8 c.c.	7·5 c.c.
Acetic acid 50 per cent.	20 grms.	20 grms.
Make up to	1000 grms.	

Light blues = Dark blue reduced 5 : 1, keeping up the acetic acid to 20 grms./litre.

Print on Naphthol A.S. prepare—12 grms./litre.

After printing, all the foregoing are passed through a soda solution, containing 10–12 grms. soda-ash per litre, at 80°–85° F., then washed and soaped at the boil, etc., as usual. The stronger soda bath used here facilitates the full development of the colours and is not harmful to other Azoic colours printed at the same time.

Naphthol A.S. Colours Printed with Vat Colours.—The usefulness of the Naphthol A.S. colours, in calico printing, would have been very much curtailed had it not been possible to print other types of colouring matters, in multicolour combinations, along with diazo solutions on Naphthol A.S. prepares.

Dark, medium, and moderately light shades of Naphthol A.S. colours present no difficulty but, for all practical purposes, it is hopeless to attempt to obtain satisfactory *pale* shades of the same colours by diluting the diazo solutions. Such dilute solutions are very unstable ; they decompose rapidly in printing, and when printed they couple slowly and unevenly with the naphthol on the cloth and the colours they eventually yield are poor and irregular in shade and inferior in fastness. Further, many colours in great demand for multicolour patterns—bright greens, various shades of blue, purple and violet, fawns, greys, and quiet mode shades—are missing from the Naphthol A.S. range. Hence the necessity for supplementary colours to fill in the gaps.

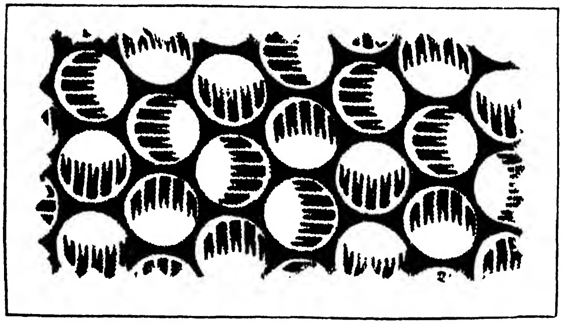
For fast work, the vat colours (and Indigosols) serve this purpose admirably. For more ordinary work, Chrome and Basic colours come into consideration.

All vat colours employed for printing, from the darkest shades to the lightest, may be printed in multicolour patterns along with diazo solutions on Naphthol A.S. prepares without modification of the usual printing colour recipes, or any alteration in the ordinary vat colour process. The Azoic colours are unaffected by the short steaming necessary to fix the vat colours, and the latter come out better, if anything, on naphthol prepares than on plain cloth.

The simultaneous printing of Vat and Azoic colours is limited, however, to patterns composed of " floating " objects, *i.e.* of colour units separated from each other by a space (if ever so narrow) of unprinted cloth. In closely

fitting patterns, where the edges of the units touch or overlap, halos are formed owing to the mutually destructive action exercised when the two chemically opposed types of colours fall together on the same spot.

A similar destructive action is liable to occur in printing when colour is unavoidedly transferred from the printed cloth to the roller next following and thence into the colour-box. To minimise this as much as possible it is advisable to work the diazo colours before the Rongalite-potash vat colours, as the latter are less affected by the former than *vice versa*. The interposition of a starch roller (*q.v.*) is also beneficial when the diazo-colour rollers are heavily engraved. In the case of Azoic colour blotches with heavy Vat colours working before them, it is *necessary* to employ a starch roller to remove loose colour from the cloth before it reaches the blotch roller.



Naphthol A.S. colour printed with Indanthrene colours (I.G.).

PREPARE.

Naphthol A.S.-D., 10 grms./litre.

PRINTING COLOURS.

Red.

35	grms.	Fast Scarlet Salt R.
465	,,	water 80° F.
500	,,	neutral starch-tragacanth thickening.
1000		

Green.

30	grms.	Indanthrene Brilliant Green G.G. double paste fine.
80	,,	glycerine.
200	,,	starch-tragacanth paste.
300	,,	British gum thickening 1 : 1.
50	,,	potassium carbonate.
30	,,	Dissolving Salt B.
60	,,	Rongalite C.
250	,,	water.
1000		

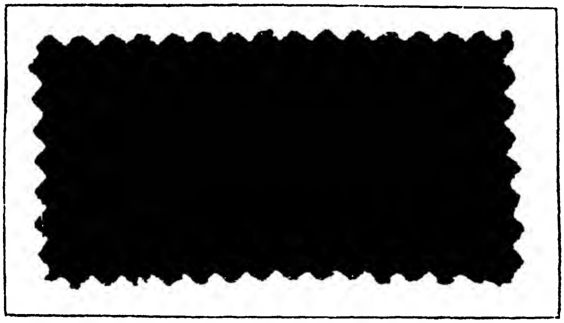
Blue.

50	grms.	Indanthrene Blue G.C.D. double paste fine.
80	,,	glycerine.
60	,,	potassium carbonate.
200	,,	starch-tragacanth paste.
300	,,	British gum thickening 1 : 1.
60	,,	Rongalite C.
250	,,	water.
1000		

After printing, the goods are steamed 4–5 minutes in moist air-free steam at 212°–216° F., then chromed (if necessary), washed in cold water, and finally soaped at the boil, washed again, and dried.

Caledon, Ciba, and Cibanone colours, etc., may all be applied, by their appropriate recipes, in exactly the same manner as above.

Naphthol A.S. Colours Printed with Indigosols.—In contradistinction to ordinary vat colours, Indigosols printed alongside Naphthol A.S. colours, either by the nitrite or the steaming process, produce no halos when their edges come in contact with those of the adjacent Azoic colours. In the nitrite process, particularly, the colours are fully developed and clearly defined at the points of junction; if by chance they overlap, due to misfitting in printing, the shades are merely modified (not destroyed) in the way usual with superposed colours. In the steaming process some loss of colour may occur where the contours touch if the Naphthol A.S. colour is weak to chlorine —otherwise the process yields satisfactory results.



Naphthol A.S. colours printed with Indigosols (I.G.).

The attached pattern, executed by the *nitrite process*, will illustrate the use of Indigosols for filling in the gaps in the Naphthol A.S. range.

PREPARE.

Naphthol A.S.-T.R., 15 grms./litre.

PRINTING COLOURS.

Orange.

10 grms. Fast Orange G.C. base.
50 ,, hot water.
12 c.c. hydrochloric acid 32° Tw.

Dissolve and add—

200 c.c. cold water.

And then—

25 ,, water.
4·6 grms. sodium nitrite.
500 ,, starch-tragacanth paste.
10 ,, sodium acetate.

To 1000 grms.

Bordeaux.

11 grms. Fast Red B. base.
15 ,, hot water.
4·8 ,, sodium nitrite.

Make into a paste and add to—

200 c.c. cold water.
18·7 ,, hydrochloric acid 32° Tw.

Allow to react 15 minutes, then add—

500 grms. starch-tragacanth paste.
10 ,, sodium acetate.

To 1000 grms.

Black.

60	grms.	Fast Black Salt K.
90	,,	acetic acid 50 per cent.
350	,,	water.
500	,,	starch-tragacanth paste.
1000		

INDIGOSOL COLOURS.

	Blue.	Green.	Grey.
Indigosol O. 4 B.	30 grms.	..	..
,, O.	5 ,,	..	..
,, Green I.B.A. paste	..	35 grms.	..
,, Printing Black I.B.	..	..	15 grms.
Glyecine A.	50 ,,	50 ,,	30 ,,
Water	355 ,,	355 ,,	400 ,,
Starch-tragacanth paste	500 ,,	500 ,,	500 ,,
Sodium nitrite	20 ,,	20 ,,	15 ,,
Water	30 ,,	30 ,,	30 ,,
Ammonia 25 per cent.	10 ,,	10 ,,	10 ,,
		1000 grms. each	

Prepare, dry, print and, after drying, sour in the open width for about 20 seconds through a bath of

20 c.c. sulphuric acid 168° Tw. } per litre.
10 ,, formic acid 90 per cent. }

Wash thoroughly after souring and soap at the boil in—

2	grms.	soap.
3	c.c.	caustic soda 62° Tw.
1000	,,	water.

Wash and dry.

The addition of formic acid to the developing bath prevents evolution of nitrous fumes and also has a beneficial effect on the purity of the white ground; the caustic soda soaping is necessary to remove traces of Indigosol dyestuff which fix on and stain the background.

If the *steaming process* is preferred, the following general recipe may be taken as a guide to the preparation of the Indigosol printing colours.

PRINTING COLOUR.

40–80	grms.	Indigosol dyestuff.
5	,,	ammonia 25 per cent.
320	,,	water.
400	,,	starch-tragacanth paste.

Mix, heat to 140° F., cool, and add—

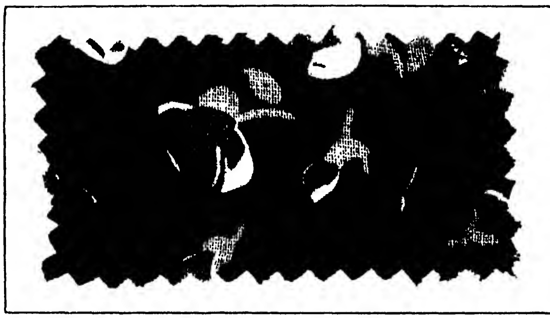
5	grms.	ammonia 25 per cent.
50	,,	ammonium oxalate (ground).
60	,,	sodium chlorate 1 : 2.
80	,,	ammonium vanadate 1 : 1000.
To 1000	grms.	

Print on Naphthol A.S. prepare, steam 5 minutes in a rapid ager, wash, and soap at the boil.

Any desired combination of Indigosols and Azoic colours may be obtained by varying the naphthols, bases, and Indigosols in either of the foregoing processes.

Naphthol A.S. Colours Printed with Chrome and Basic Colours.—The methods of printing Basic and Chrome colours in combination with Naphthol A.S. colours are identical with those already described in the section "Azoic Colours with Steam Colours" (page 521). The printing colours in both cases are made-up in accordance with the usual recipes for steam colours, a little extra organic acid being added, if necessary, to neutralise the alkalinity of the naphthol prepares.

The Basic colours are chiefly employed in the production of shipping styles for the East, where brightness is of more importance than fastness. In these styles they take the place of vat colours for the production of bright shades of yellow, green, light blue, violet, etc., and whilst not particularly fast they are yet sufficiently so to withstand the soaping that is necessary for the removal of superfluous naphthol from the unprinted portions of the fabric. The Chrome colours may be used for any class of work not required to be of extreme fastness, but still of good fastness to washing and fairly good to light.



Naphthol A.S. colours printed along with Basic colours (I.G.).

The above pattern illustrates the use of a Basic green in an otherwise fast print.

PREPARE.

Naphthol A.S., 15 grms./litre.

PRINTING COLOURS.

Orange.

45	grms.	Fast Orange Salt G.R.
435	,,	water at 80–85° F.
500	,,	starch-tragacanth paste.
20	,,	acetic acid 50 per cent.
1000		

Blues.

	Light.	Dark (blotch).
Variamine Blue Salt B.	8 grms.	20 grms.
Acetic acid 50 per cent.	20 ,,	20 ,,
Water	472 ,,	460 ,,
Starch-tragacanth paste	500 ,,	500 ,,
	1000 grms.	

Green.

15	grms.	Thioflavine T.
3	,,	Brilliant green N. crys.
30	,,	glycerine.
130	,,	acetic acid 50 per cent.
20	,,	Acetine N.
2	,,	tartaric acid.
200	,,	water.

Dissolve and add to—

500 grms. starch-tragacanth paste.

Add—

50	,,	tannic acid.
50	,,	acetic acid 50 per cent.
1000		

Print, dry, steam for 4–5 minutes in fairly dry steam, and fix in—

5–10	grms.	tartar-emetic	at 120° F.
10–20	,,	chalk	
1000	,,	water	

Wash, soap at about 120° F., wash, and dry.

If Chrome colours alone are printed in combination with Azoic colours, the tartar-emetic treatment is replaced by a simple chalk bath, or even a wash, before soaping.

Brenthols.—In all the foregoing processes the Brenthols, manufactured by British Synthetics, Ltd., may be substituted for the A.S. Naphthols without the slightest alteration in formulæ or any modification of *modus operandi*. For convenience of reference the equivalents in the two series, which differ only in name, are given below :—

Naphthol	A.S.	is equivalent to Brenthol	A.S.
,,	A.S.-G.	,, ,, ,,	A.T.
,,	A.S.-B.O.	,, ,, ,,	A.N.
,,	A.S.-D.	,, ,, ,,	O.T.
,,	A.S.-O.L.	,, ,, ,,	F.R.
,,	A.S.-R.L.	,, ,, ,,	P.A.
,,	A.S.-B.G.	,, ,, ,,	F.O.
,,	A.S.-B.S.	,, ,, ,,	M.N.
,,	A.S.-T.R.	,, ,, ,,	C.T.
,,	A.S.-S.W.	,, ,, ,,	B.N.
,,	A.S.-B.R.	,, ,, ,,	D.A.
,,	A.S.-E.	,, ,, ,,	B.B.
,,	A.S.-L.B.	,, ,, ,,	B.T.
,,	A.S.-S.G.	,, ,, ,,	G.B.
,,	A.S.-L.T.	,, ,, ,,	M.A.
,,	A.S.-G.R.	,, ,, ,,	N.G.
,,	A.S.-S.R.	,, ,, ,,	R.B.
,,	A.S.-I.T.R.		No equivalent
	No equivalent	,,	B.A.

So far as the English market is concerned the above equivalent products are identical in origin, manufacture, and properties, and may be used interchangeably in any recipe or process.

The Rapid Fast Colours.—The problem of producing Azoic colours directly on the fibre without previous preparation of the cloth with naphtholates was

industrially solved by the Chemische Fabrik Griesheim-Elektron who, in 1914–1915, introduced the first members of the now important series of Rapid Fast Colours.

These colours contain in themselves the two components essential to the formation of an Azoic colour, and they are printed on *unprepared* cloth. After printing they are fixed by steaming in the rapid ager, or by hanging, and finally developed by a short passage through a bath of dilute organic acids, followed by washing and soaping at the boil.

The Rapid Fast Colours are mixtures of the nitrosamines of various Fast Colour Bases with, except in one instance, the alkali salts of Naphthol A.S. and its congeners. In this respect they resemble older analogous mixtures of β-naphthol and paranitraniline (already alluded to in connection with the latter), but they are far more stable and much more valuable for printing and dyeing purposes. They are prepared in both paste and powder forms, and in both they possess considerable stability, keeping for long periods if protected from acid vapours and undue exposure to air. The carbon dioxide of the air gradually neutralises the causticity of the mixtures, liberating free naphthol which couples-up with the diazo content and thereby causes premature development of the colour and, consequently, deterioration. All Rapid Fast Colour containers must, therefore, be kept well closed in storage.

The Rapid Fast Colours, in their finished state, are identical in chemical composition and structure with the colours obtained by printing diazo solutions on Naphthol A.S. prepares, and prints obtained by their means are of excellent fastness to washing and chlorine, and most of them in medium and full shades are also of very good fastness to light. Rapid Fast Blue B. is of only moderate fastness to light, but it may be improved by an after-treatment with copper sulphate and acetic acid.

The list of Rapid Fast Colours given below includes all those in current use and, although frequent additions are made to the range, it will serve to give an idea of the scope of the series :—

Rapid Fast Yellow G.G.H. powder.
,, ,, ,, G.H. conc. paste and powder.
,, ,, Orange R.G. paste and powder.
,, ,, ,, R.H. ,, ,, ,,
,, ,, ,, G.H. powder.
* ,, ,, Scarlet L.H. paste and powder.
,, ,, ,, G.H. ,, ,, ,,
,, ,, ,, R.H. powder.
* ,, ,, Red 3 G.L. paste.
* ,, ,, ,, G.L. paste and powder.
,, ,, ,, R.H. ,, ,, ,,
* ,, ,, ,, L.B. paste.
,, ,, ,, I.R.H. powder.

Rapid Fast Red B. paste and powder.
,, ,, ,, B.B. ,,
,, ,, ,, F.G.H. powder.
* ,, ,, Bordeaux B. paste and powder.
,, ,, ,, I.B. ,, ,, ,,
,, ,, ,, R.H. powder.
* ,, Brown G.G.H. ,,
,, ,, ,, B.H. ,,
,, ,, ,, I.R.H. ,,
,, ,, Olive Brown I.G.H. powder.
*Rapidogen G. paste double conc.
Rapid Fast Blue B. paste and powder.

Printing colours containing Rapid Fast Colours designated by the letter "H" keep in good working condition for several days; those marked * are particularly fast to light. The powder brands are twice the strength of the corresponding pastes and are more convenient and reliable in use, as they do not dry-up in storage.

In preparing the printing colours the *paste* brands are simply mixed with tepid water to a smooth cream and stirred into the thickening paste; the *powder* brands are first pasted up with a little caustic soda and water before mixing with the thickening. Rapidogen G., with addition of an appropriate naphthol, is prepared similarly.

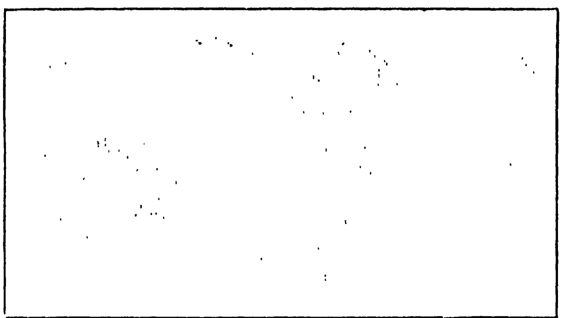
When Rapid Fast Colours, either alone or printed in combination with Vat, Chrome, Indigosol, or Basic colours, are to be fixed by steaming, an

addition of neutral sodium chromate is made to the printing colour for the purpose of increasing resistance to the influence of steam. With this addition the goods may be steamed in a rapid ager without sensible alteration of the colours.

When medium and pale pinks of Rapid Fast Red R.H. and Rapid Fast Red L.B. are printed, or when reductions of other strong printing colours are made, it is necessary to add 5–10 grms. caustic soda 62° Tw. and 25–50 grms. neutral chromate solution to every 1000 grms. of printing colour. A similar addition of caustic soda is also advisable in the case of several other colours of full printing strength, notably Rapid Fast Blue B., Rapid Fast Reds B. and B.B., and Rapid Fast Bordeaux B.; the little extra causticity improves the stability of the printing colours.

Like all Naphthol A.S. combinations, the Rapid Fast Colours may be supplemented with colours of other groups, and they also find many applications in various mixed resist and discharge styles.

The following recipes and patterns illustrate the use of these colours in direct printed styles :—



Rapid Fast Yellow G.G.H. powder, 3 and 1 per cent. (I.G.).

Rapid Fast Yellow G.G.H. Powder Printing Colour.

30 grms. Rapid Fast Yellow G.G.H. powder.
30 ,, caustic soda 62° Tw.
30 ,, warm water.

Mix to a paste and add—

360 grms. warm water 75°–80° F.
500 ,, starch-tragacanth paste (neutral).
50 ,, neutral chromate solution.

1000

Light Yellow.

1 part above yellow.
2 parts reduction paste for Rapid Fast Colours.

A similar yellow using Rapidogen G. is made-up with Naphthol A.S.-G., A.S.-R.L., or A.S.-B.G., thus :—

Rapidogen G. Printing Colour.

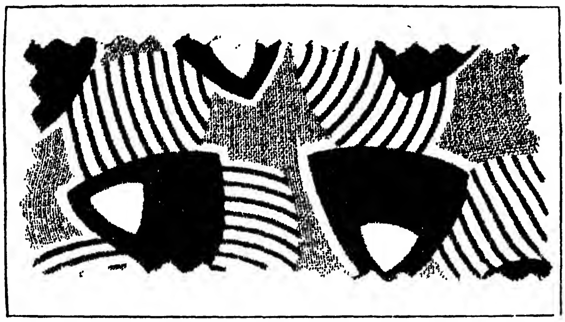
60 grms. Rapidogen G. paste dble. conc.
30 ,, Monopol Brilliant Oil.
24 ,, Naphthol A.S.-G. (or 20 grms. A.S.-R.L. or A.S.-B.G.).

Mix to a cream with a little water and dissolve in—
386 grms. warm water 75°–80° F.

Then add to—
500 grms. neutral starch-tragacanth paste.

1000

This yellow gives the same shade as a printing colour containing 80 grms. Rapid Fast Yellow G.H. per kilogramme.

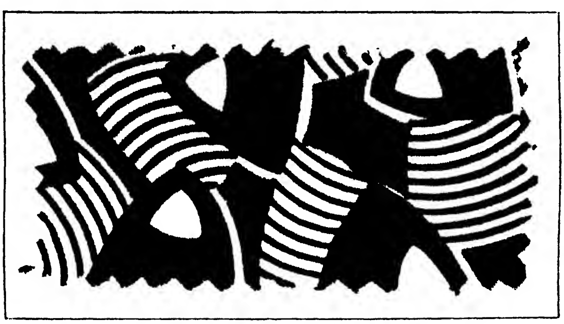


Rapid Fast Orange R.H. powder, 6 and 2 per cent. (I.G.).

RAPID FAST ORANGE PRINTING COLOUR.

60	grms.	Rapid Fast Orange R.H. powder.
30	,,	caustic soda 62° Tw.
20	,,	Monopol Brilliant Oil.
50	,,	neutral chromate solution.
340	,,	warm water 75°–80° F.
500	,,	starch-tragacanth.
1000		

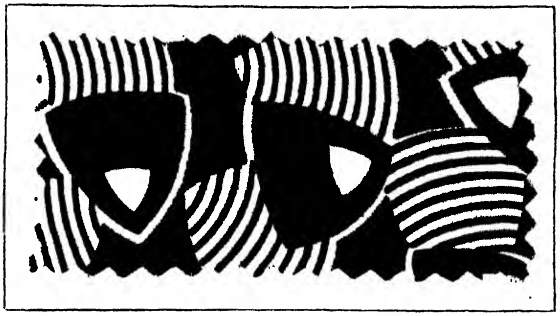
Light Orange = reduced 1 : 2, as for Yellow.



Rapid Fast Red I.R.H. powder, 6 and 2 per cent. (I.G.).

Red / Light red } recipes as for Orange, above.

The next patterns are printed with Rapid Fast Colours in paste form.



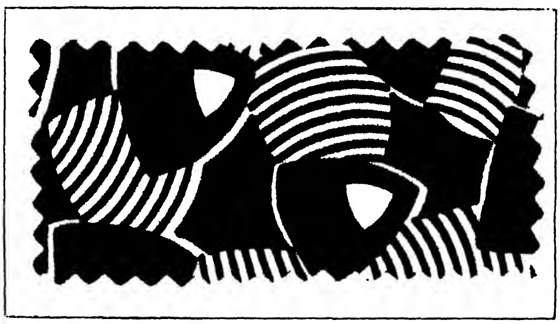
Rapid Fast Bordeaux I.B. paste, 12 and 4 per cent. (I.G.).

RAPID FAST BORDEAUX PRINTING COLOUR.

120	grms.	Rapid Fast Bordeaux I.B. paste.
30	,,	Monopol Brilliant Oil.
300	,,	cold water.
50	,,	neutral chromate solution.
500	,,	neutral starch-tragacanth paste.
1000		

Light shade = reduced 1 : 2.

The extra 1 per cent. caustic soda 62° Tw. added to the following blue recipe is necessary to maintain its stability in printing.



Rapid Fast Blue B. paste, 12 and 4 per cent. (I.G.).

RAPID FAST BLUE PRINTING COLOUR.

120	grms.	Rapid Fast Blue B. paste.
10	,,	caustic soda 62° Tw.
30	,,	Monopol Brilliant Oil.
50	,,	neutral chromate solution.
290	,,	cold water.
500	,,	neutral starch-tragacanth paste.
1000		

Light shade = reduced 1 : 2.

REDUCTION PASTE FOR RAPID FAST COLOURS.

500	grms.	neutral starch-tragacanth paste.
470	,,	water.
5	,,	caustic soda 62° Tw.
25	,,	neutral chromate solution.
1000		

NEUTRAL CHROMATE SOLUTION.

150	grms.	sodium bichromate, crys.
700	,,	water.
150	,,	caustic soda 62° Tw.
1000		

The goods printed with the foregoing Rapid Fast Colours are steamed for 2–4 minutes at 212° F. in the rapid ager and then passed at 160°–175° F. through a bath containing—

30 c.c. acetic acid 12° Tw. (or formic acid 90 per cent.),
25 grms. Glauber's salt,
per litre,

the temperature of the bath being kept about constant and the liquid replenished frequently to keep up its acidity. This souring may be carried out in a small beck or trough running in connection with a washing and soaping range. In any case, after washing, the goods are best soaped at the boil in a rope soaper, an operation which enhances the brilliancy and improves the fastness of the colours.

If the goods are hung instead of steamed, the addition of neutral chromate to the printing colours is unnecessary except in the case of Rapid Fast Blue B., which develops better in the presence of chromate. The printed pieces are hung for 12–14 hours in a moist and moderately warm hanging room, after which they follow the same process as steamed goods.

Another method of developing Rapid Fast Colours is to steam the printed goods in an atmosphere of acetic acid. For this purpose almost any sort of closed chamber is suitable; all that is required is a simple means of evaporating acetic acid, a supply of steam and a system of rollers for carrying the cloth through the chamber, which may be of wood, iron, or asbestos board. In this manner development is effected, to a certain extent, in a single operation. For cheap goods the colours are sufficiently developed to permit of subsequent washing and soaping being omitted; but if the brightest and fastest results are required, the goods must be washed and soaped at the boil. As already noted, a boiling soap treatment is *imperative* for the full development of the correct shade of many Naphthol A.S. combinations—it is an integral part of the process.

Some of the newer Rapid Fast Colours may be developed (without steaming or hanging) in the same manner as Rapidogen dyestuffs by the *drying cylinder process*, which consists in padding the dry printed pieces with cold acetic-formic acid and drying on heated cylinders; or alternately, by the wet developing process, in which the dried but unsteamed prints are passed through an almost boiling bath of acetic-formic acid-Glauber's salt for about 20 seconds. In both cases the usual washing and boiling soap treatment follows.

The Rapid Fast Colours printed alongside, and in admixture with, Indigosols.—Rapid Fast Colours and Indigosols may be printed together in multicolour patterns by either the steaming or nitrite process.

For the *steaming process* the recipes already given for both groups of colours are employed, and the treatment after printing follows the usual routine of steaming for 6–8 minutes to develop the Indigosols, followed by an acetic acid-Glauber's salt bath at 160°–175° F. to develop the Rapid Fast Colours. The process is confined to the printing of individual colours of each group and *does not allow* of the two types of colours being mixed together.

In the *nitrite process* the Indigosols and Rapid Fast Colours exert no influence on each other's development and may be mixed together in any proportions for the production of a number of green, violet, brown, etc., shades which are missing from their respective individual ranges ; even a good fast black may be obtained from such mixtures. All the Indigosols are available, either as individual printing colours or for shading Rapid Fast Colours ; but for the latter purpose the blues are naturally the most important and of these, the O. 4 B. and O. brands are the most generally useful. Rapid Fast Colours for compound shades are selected from those of which the made-up printing colours are of good stability. The preparation of compound shades of green, brown, olive, etc., follows the usual colour-shop methods of mixing standard colours together.

STANDARD COLOURS.

	YELLOW G.H.	ORANGE R.H.
Rapid Fast Yellow G.H. powder	100 grms.	..
,, ,, Orange R.H. powder	..	75 grms.
Caustic soda 62° Tw.	37·5 ,,	30 ,,
Monopol Brilliant Oil	20 ,,	20 ,,
Cold water	..	345 ,,
Water at 120°–140° F.	312·5 ,,	..
Starch-tragacanth paste	500 ,,	500 ,,
Neutral chromate solution	30 ,,	30 ,,
	1000 grms. each.	

BLUE O. 4 B.

100 grms. Indigosol O. 4 B.
350 ,, boiling water.
500 ,, starch-tragacanth paste (slightly alkaline).

950

The necessary nitrite of soda is added just before printing ; it is adjusted to the quantity of Indigosol O. 4 B. in any mixture, but ought not to fall below a minimum of 10–15 grms. per kilo. of printing colour: 100 grms. Indigosol require 50 grms. $NaNO_2$.

EXAMPLES OF MIXTURES.

	GREEN.	DARK GREEN.	OLIVE.	BROWN.	FAWN.
Yellow G.H.	800	400	745	..	350
Orange R.H.	..	..	50	800	500
Blue O. 4 B.	160	545	160	160	120
Sodium nitrite 1 : 2	40	55	45	40	30

Lighter shades may be obtained by adding more thickening, or better, the following reducing paste :

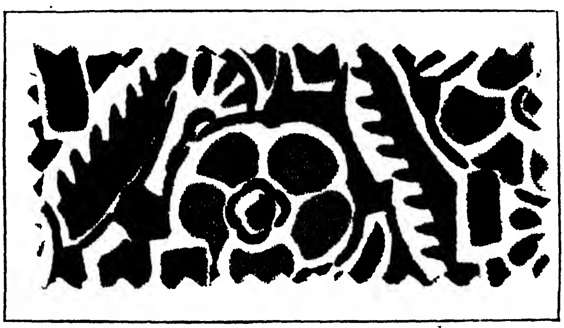
Reducing Paste (Indigosol-Rapid Fast Colour Mixtures).

1000 grms. Neutral starch-tragacanth paste.
2 c.c. caustic soda 50° Tw.
10 grms. sodium nitrite.

Very dark shades require to be made-up separately as required and are better prepared as freshly as possible. The black below is very stable for a Rapid Fast Colour combination.

	Dark Purple.	Black.
Rapid Fast Bordeaux B. paste . .	50 grms.	..
,, ,, Orange R.H. paste . .	..	100 grms.
Monopol Brilliant Oil	20 ,,	20 ,,
Caustic soda 62° Tw.	15 ,,	..
Cold water	115 ,,	..
Water at 75°–85° F.	..	80 ,,
Indigosol O. 4 B. (pure colour) . .	..	100 ,,
Neutral starch-tragacanth paste . .	500 ,,	300 ,,
Standard Blue O. 4 B. (p. 566) . .	230 ,,	..
,, Yellow G.H. (p. 566) . .	..	330 ,,
Sodium nitrite solution 1 : 2 . .	40 ,,	..
Sodium nitrite (crystals) . . .	..	50 ,,
Neutral chromate solution . . .	30 ,,	20 ,,
	1000 grms. each.	

A black may also be obtained according to the recipe given for the following pattern ; it is a pure Azoic black.



Rapid Fast Colours and Indigosols, and a mixture of the two (Green) (I.G.).

Printing Colours.

Red.

60 grms. Rapid Fast Scarlet G.H. paste.
20 ,, Monopol Brilliant Oil.
10 ,, caustic soda 62° Tw.
410 ,, water.
500 ,, tragacanth mucilage.

1000

Black.

126	grms.	Rapid Fast Blue B. paste.
30	,,	Monopol Brilliant Oil.
4	,,	Naphthol A.S.-G.
290	,,	water.
500	,,	tragacanth mucilage.
50	,,	neutral chromate solution.
1000		

Green.

45	grms.	Rapid Fast Yellow G.H. powder.
15	,,	Indigosol O. 4 B.
30	,,	caustic soda 62° Tw.
230	,,	water 120°–140° F.
600	,,	tragacanth mucilage.
50	,,	neutral chromate solution.
30	,,	nitrite of soda solution 1 : 2.
1000		

Violet.

20	grms.	Indigosol Violet A.Z.B.
330	,,	water.
10	,,	caustic soda 62° Tw.
600	,,	tragacanth mucilage.
30	,,	sodium nitrite solution 1 : 2.
10	,,	ammonia 25 per cent.
1000		

After the goods are printed, on *unprepared* cloth, with the foregoing colours, they are steamed for 3 minutes at 212° F. in a rapid ager (or alternatively, hung overnight in a warm moist atmosphere), and then passed for at least 15 seconds through a hot acid bath containing—

40 c.c. formic acid 90 per cent.⎫
80 grms. common salt ⎭ per litre,

or better, 30 grms. oxalic acid per litre,

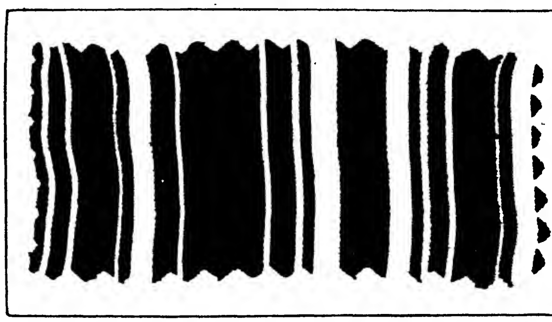
at 180°–200° F., which temperature must be maintained to ensure satisfactory results. The ordinary acetic acid bath used for Rapid Fast Colours printed alone is not sufficiently strong to develop the Indigosols. After souring, the goods are washed and soaped at the boil as usual. The whole of these developing, washing, and soaping operations may be carried out in an open soaping range, one passage through which is usually sufficient to give a good white, full colours, and good fastness to rubbing.

Rapid Fast Colours printed alongside Vat Colours.—Owing to their excellent all-round fastness several of the red, scarlet, and Bordeaux brands of the Rapid Fast Colours lend themselves admirably to the production of very fast multicolour prints in association with Indanthrenes, Caledons, and other vat colours. They are brighter in shade and simpler to prepare for printing than the corresponding shades of vat colours and, as they are also cheaper and practically as fast, they constitute efficient and economical substitutes for the more expensive Indanthrene and Caledon dyestuffs. On economy grounds,

too, orange and yellow shades are often obtained from Rapid Fast Orange R.H. and Rapid Fast Yellow G.H. in preference to vat yellows and oranges.

For fast styles which are *not required to withstand the action of chlorine*, the Sulphur colours may also be used for multicolour printing along with Rapid Fast Colours. In this connection Thional Brilliant Blue G. and Thional Brilliant Green 3 G. (Sandoz) are particularly suitable when printed by Cheshire's process (*q.v.*). On the whole, however, the Sulphur colours, pure and simple, are neither bright enough nor fast enough to satisfy present-day requirements, and find but little application in modern styles. On the contrary, sulphurised vat dyestuffs of the Hydron Blue R., Hydron Black C., and Indocarbon C.L. types possess excellent all-round fastness and are extensively employed in the printing of fast vat and Azoic colour styles.

Rapid Fast Colours and Vat (or Sulphur) colours are printed together without modification of their usual recipes, and by a process which differs but little from those in use for each separately—the difference being a combined developing bath of sodium bichromate for the vat colours, and acetic acid for the Rapid Fast Colours.



Rapid Fast Red and Hydron Black C. "Supratix" (I.G.).

Printing Colours.

Red.

50	grms.	Rapid Fast Red R.H. paste.
70	,,	,, ,, Scarlet L.H. paste.
20	,,	Monopol Brilliant Oil.
330	,,	water.

Mix and add—

500	,,	starch-tragacanth paste.
30	,,	neutral chromate solution.
1000		

Black.

50	grms.	Hydron Black C. "Suprafix."
60	,,	methylated spirit 1 : 1.

Make into a fine paste and add—

100	grms.	caustic soda 76° Tw.
30	,,	soda-ash.
185	,,	water.
450	,,	thickening B.W.S.
100	,,	glucose.

Warm to 140° F., cool, and add—

25	grms.	Rongalite 1 : 1.
1000		

THICKENING B.W.S.

280	grms.	British gum.
100	,,	wheat starch.
20	,,	Dissolving Salt B.
600	,,	water.
1000		

Boil and cool.

The goods printed with the foregoing colours are steamed for 5 minutes at 212°–216° F. in moist air-free steam and then developed in a hot bath of

1–2	grms.	sodium bichromate,
30	c.c.	acetic acid 50 per cent.,
25	grms.	sodium sulphate,
per 1000	c.c.	water,

at 175° F., washed, soaped at the boil, washed, and dried.

All colours of the two groups may be applied similarly.

Rapid Fast Colours with Basic and Chrome Colours.—Mixed colourings containing Rapid Fast, Basic, and Chrome mordant colours may be printed without difficulty, and without formation of halos where adjacent contours touch, provided that the Basic and Chrome colours are neutral or at least contain a minimum of acid—not more than 2½–3 per cent. The two following examples illustrate suitable general recipes for Chrome and Basic colours.

BASIC COLOUR.

25	grms.	Basic dyestuff.
50	,,	Fibrit D.
50	,,	methylated spirit.
155	,,	water.
520	,,	British gum-starch paste.
100	,,	tannic acid.
100	,,	methylated spirit.
1000		

CHROME COLOUR.

30	grms.	Modern heliotrope (D. & H.).
200	,,	boiling water.
635	,,	starch-tragacanth paste.
25	,,	acetic acid 60 per cent.
100	,,	chromium acetate 24° Tw.
3	,,	Rongalite C.
7	c.c.	water.
1000		

After printing, the goods are steamed for 5 minutes at 212° F. in a rapid ager, then given a ½–1 minute passage through a warm bath of

10	grms.	tartar-emetic,	per litre
25	,,	Glauber's salt,	
10	c.c.	acetic acid 50 per cent.,	

at 160° F., and finally washed, soaped at 160° F., washed, and dried.

When Basic colours are absent from the colour combination, the tartar-emetic is omitted.

Rapid Fast Colours with Aniline Black.—Not all Rapid Fast Colours nor all Aniline blacks are suitable for printing together. The best results are obtained by using vanadium or copper sulphide blacks along with the following brands of Rapid Fast Colours:

Rapid Fast Yellow G.H.	Rapid Fast Scarlet L.H.
,, ,, ,, G.G.H.	,, ,, ,, G.H.
,, ,, Orange R.H.	,, ,, Red R.H.

General Recipe for Rapid Fast Colours.

100-150	grms.	Rapid Fast Colour in paste.
20	,,	Monopol Brilliant Oil.
30	,,	Ludigol.
350-300	,,	cold water.
500	,,	neutral starch-tragacanth paste.
1000		

The Ludigol (*m*-nitrobenzene sulphonate of soda) in this recipe replaces neutral chromate of soda as a preservative against the influence of steam.

Ferrocyanide aniline blacks are altogether unsuitable for printing with Rapid Fast Colours, as the various gases they evolve during steaming exercise a destructive action on the undeveloped colours. Copper sulphide and vanadium blacks are free from this defect, and any *well balanced* recipe of either may be utilised with safety. The two following recipes, recommended by the makers of Rapid Fast Colours (The I. G. Farbenindustrie A. G.), are taken from practice:

Vanadium Aniline Black.

200 grms. wheat starch.
500 ,, water.

Boil and add—

35 grms. sodium chlorate.

Cool and add—

115 grms. water.
75 ,, aniline oil.
70 ,, hydrochloric acid 36° Tw.

Immediately before use add—

5 grms. vanadate of ammonia 1 : 1000.

1000

For general work the amount of starch might be reduced to 150 grms. per kilo. or a portion of it replaced by British gum, which imparts a better working quality to Aniline blacks.

Copper Sulphide Aniline Black.

I	250	grms.	light British gum. } boil and add:
	280	,,	water. }
	34	,,	sodium chlorate.
II	94	,,	aniline salt.
	12	,,	aniline oil.
	180	,,	water.
III	25	,,	Chrome yellow paste 40 per cent.
	25	,,	copper sulphide paste 30 per cent.
	20	,,	potassium sulphocyanide.
	10	,,	Methyl violet solution 10 per cent. (for sightening).
To	1000		

Prepare I, II, and III separately and mix them together just before printing. For heavy patterns the black is reduced 3 : 1 or even 2½ : 1.

After printing and drying, the goods are preferably hung for 12 hours, or overnight, in a moderately warm hanging room ("stove"); they are then steamed for about 3 minutes in an Aniline black ager with the ventilator full open and passed at 180°–195° F. through a combined oxidising and developing bath set with :

$$\left.\begin{array}{ll} \text{20 c.c.} & \text{acetic acid 50 per cent.} \\ \text{2 grms.} & \text{sodium bichromate} \end{array}\right\} \text{per litre,}$$

after which they are washed, soaped at 180° F., washed, and dried.

Aniline blacks in association with Rapid Fast yellows, oranges, and reds are used mainly for the printing of relatively large-scale patterns, containing heavy masses of black, or with black grounds, on raised cotton fabrics and cotton velvet. They are much cheaper than vat or Azoic colour blacks for heavy styles, and though they are liable to form halos in close-fitting patterns, this tendency can be more or less overcome by careful attention to the consistency of the printing colours, to the engraving of the contours of the colour masses and to the expeditious drying of the printed material.

Rapidogen Colours.—An important recent development in the direct production of Azoic colours on the fibre is embodied in the Rapidogen series of dyestuffs which, whilst closely related to the Rapid Fast colours in composition, purpose, general properties, and mode of application, are yet characterised by *extraordinary stability*—a stability much superior, in every way, to that possessed by the Rapid Fast colour group.

The Rapidogen colours of the I. G. Farbenindustrie A. G. consist of mixtures, in powder form, of naphthols of the A.S. range with soluble diazo-amides obtained by combining various diazotised Fast Colour bases with amino-fatty acids. An amide of this type, made from *p*-nitro-*o*-anisidine and methylaminoacetic acid (sarcosine) and afterwards neutralised, is represented by the formula :

$$C_6H_3(NO_2)OCH_3.N=N.N(CH_3).CH_2.COONa$$

The Rapidogens are readily soluble in dilute caustic soda and, when thickened, they give, as already stated, printing colours of excellent stability. On subjecting the printed goods to a hot acid treatment, the diazo-amide is split up and the diazo component thus liberated couples at once with the naphthol component.

Another advantage of the Rapidogen colours is that they may be fully developed without the necessity for steaming or for hanging overnight in warm air ; all they require is an acid after-treatment.

In the so-called *Wet Developing Process*, the goods, after printing and drying, are passed directly through an almost boiling bath of mixed acetic and formic acids and then, at once, washed and soaped at the boil. If, however, the Rapidogen colours are printed in combination with Vat colours, Indigosols, Basic and Chrome colours, Aniline black, etc., they may be steamed without detriment before passing into the acid developing bath. In some cases a short steaming results in rather fuller shades being obtained.

The *Acid-Steam Developing Process*, extensively used in practice for Rapid Fast colours, has been found equally suitable for Rapidogen colours. As already described, the method consists in steaming the printed goods in an atmosphere of steam charged with a mixture of acetic and formic acid vapours.

In this way the colours are completely developed, at one operation, in the steamer (rapid ager) and require no further treatment beyond the usual washing and soaping. The acid-steaming method yields darker prints than those obtained by the wet developing process, and is usually preferred on the large scale when suitable apparatus is available ; otherwise, as when carried out in an ordinary iron ager, it is regarded as " more bother than worth " since, as might be expected, the acids rapidly attack the body and all internal fittings of the machine.

The *Drying Cylinder Developing Process* possesses the advantages of both the foregoing processes without the disadvantages of either ; it yields fuller prints than the wet developing process and dispenses entirely with acid-steaming or steaming of any sort when the goods are printed with Rapidogens alone. The process is operated by padding the printed goods, on the face side, between two rollers with a *cold* acetic-formic acid mixture, and then immediately drying the acid-saturated cloth over the hot cylinders of a drying machine. The colours are at once fully developed by the combined action of the heat and acids (which virtually amounts to an acid-steaming) and the goods, thereafter, require only to be washed and soaped. Developed in this way, prints retain the original sharp definition of the pattern, and in depth of shade are fully equal to those obtained by the acid-steaming process.

Working details of these alternative methods of developing will be found in the description of the printed patterns.

Printing colours of Rapidogens are prepared by pasting up or dissolving the requisite quantity of dyestuff in mixtures of caustic soda, methylated spirit, Monopol Brilliant Oil, and warm water, as indicated in the following tables, stirring the paste, so made, into the thickening and, finally, making up to the required weight with water and such other ingredients as appear in the recipes.

RAPIDOGEN PRINTING COLOURS.

Dyestuffs, etc.	Grammes.							
Rapidogen Yellow G.	80	..	..	..	..	..	..	..
,, Orange G.	..	80	..	..	..	..	..	..
,, Scarlet R.	..	..	80	..	..	..	..	..
,, Red G.	..	..	..	80	..	..	..	..
,, ,, I.R.	..	..	..	..	80	..	..	..
,, ,, R.	..	..	..	..	..	80	..	..
,, Bordeaux R.	..	..	..	..	..	..	80	..
,, Corinth R.	..	..	..	..	..	..	..	60
Caustic soda 32½ per cent. (=70° Tw.)	20	30	30	30	30	30	30	30
Methylated spirit	30	..	..	..	..	..	..	..
Monopol Brilliant Oil	..	30	30	30	30	30	30	30
Water (lukewarm)	150	150	150	150	150	150	150	150
Neutral starch-tragacanth thickening	500	500	500	500	500	500	500	500
Zinc oxide 1 : 1	50	..	..	..	..	..	..	..
Neutral chromate solution	..	..	..	..	..	..	50	..
Water (cold)	170	210	210	210	210	210	160	230
	1000 grms. each by weight.							

Dyestuffs, etc.	Grammes.								
Rapidogen Corinth I.B.	60	..	..	..	..	..	..	..	..
,, Violet B.	..	45	..	..	..	..	..	..	..
,, Blue R.	..	..	45	..	..	..	..	..	..
,, ,, B.	..	..	..	45	..	..	..	..	..
,, Green B.	..	..	..	..	60	..	..	..	..
,, Brown I.R.	..	..	..	..	..	80	..	..	..
,, Olive Brown I.G.	..	..	..	..	..	..	80	..	..
,, Brown I.B.	..	..	..	..	..	..	..	80	..
,, ,, I.R.R.	..	..	..	..	..	..	..	..	80
Caustic soda 32½ per cent. (=70° Tw.)	30	30	30	30	30	30	30	30	30
Methylated spirit	..	30	30	30	..	..	..	..	..
Monopol Brilliant Oil	30	..	..	..	30	30	30	30	30
Water (lukewarm)	150	150	150	150	150	150	150	150	150
Glyecine A.	..	..	30	50	50	..	..	..	..
Neutral starch-tragacanth thickening	500	500	500	500	500	500	500	500	500
Urea	..	..	50	50	50	..	..	..	..
Zinc oxide 1:1	..	50	50	..	..	..	..	..	..
Water (cold)	230	195	115	145	130	210	210	210	210
	1000 grms. each by weight.								

Reducing Pastes for Foregoing Colours.

	A.	B.	C.	D.	E.
	Parts.	Parts.	Parts.	Parts.	Parts.
Neutral starch-tragacanth thickening	600	600	600	600	600
Water	330	350	325	290	260
Caustic soda 32½ per cent. (=70° Tw.)	15	30	20	30	30
Methylated spirit	20	..	..	30	..
Monopol Brilliant Oil	..	20	20	..	30
Glyecine A.	..	..	..	..	30
Neutral chromate solution	..	..	35	..	..
Urea	..	..	..	..	50
Zinc oxide 1:1	35	..	..	50	..
	1000 parts each by weight.				

Paste A. is for Rapidogen Yellow G.

,, B. ,, Rapidogen Orange G., Rapidogen Scarlet R.,
,, Red G., Rapidogen Red I.R.,
,, ,, R., Rapidogen Corinth R.,
,, Corinth I.B., Rapidogen Brown I.R.,
,, Olive Brown I.G., Rapidogen Brown I.B.,
,, Brown I.R.R.

,, C. ,, Rapidogen Bordeaux R.

,, D. ,, Rapidogen Violet B.

,, E. ,, Rapidogen Blue R.
,, ,, B.
,, Green B.

Paste E. may replace paste B. with advantage, in all cases, but it is more expensive.

It is not necessary to adhere strictly to the foregoing recipes for reduction pastes, though they are recommended as being most suitable for the colours specified. For Rapidogen Yellow G. and Violet B., either paste A. or D. may be used without much difference in effect; for all other colours paste E. will generally be found satisfactory, except in the case of Bordeaux R., which requires an addition of neutral chromate of soda, both to standard colour and to reduction pastes.

Prints produced with Rapidogen dyestuffs possess excellent fastness to washing and chlorine and, in all but pale shades, good fastness to light. When pale shades are required in a colouring, they may be obtained, in the usual way, from Vat or Indigosol dyestuffs.

In respect of price the Rapidogen dyestuffs are rather more expensive than the Rapid Fast colours, the extra costs and processes entailed in manufacturing specially stable products naturally being reflected in their market price. But the slightly increased initial cost is more than counterbalanced by advantages in other directions. The colours are not affected by the carbonic acid in the air, and they may be stored for long periods, under normal conditions, without fear of deterioration. Moreover, printing colours made up from Rapidogen dyestuffs keep in good working condition for many days, whereas those prepared from Rapid Fast colours are, for the most part, useless after twenty-four hours.

The Rapidogen colours, too, give brighter shades than the Rapid Fast colours—shades as bright, in fact, as those obtained by printing diazo-solutions on naphtholated cloth, which, after all, is the best and cheapest process of printing Azoic colours when a large output is in question.

The following patterns, with details of their production, illustrate the type of colours provided by the Rapidogen series:

Rapidogen Yellow G. (I.G.).

Rapidogen Yellow G.

80	grms.	Rapidogen Yellow G.
20	,,	caustic soda 70° Tw.
30	,,	methylated spirit.
150	,,	lukewarm water.
500	,,	neutral starch-tragacanth paste.
170	,,	cold water.
50	,,	zinc oxide paste 50 per cent.
1000		

Light Yellow { 1 part above.
2 parts reducing paste A.

Rapidogen Orange G. (I.G.).

Rapidogen Orange G.

80 grms. Rapidogen Orange G.
30 grms. caustic soda 70° Tw.
30 grms. Monopol Brilliant Oil.
150 grms. lukewarm water.
500 grms. neutral starch - tragacanth paste.
210 grms. cold water.

1000

Light Orange { 1 part above. 2 parts reducing paste B. or E.

Rapidogen Red G. (I.G.).

Rapidogen Red G.

80 grms. Rapidogen Red G. made-up according to recipe for Rapidogen Orange G.

Light red { 1 part above. 2 parts reducing paste B. or E.

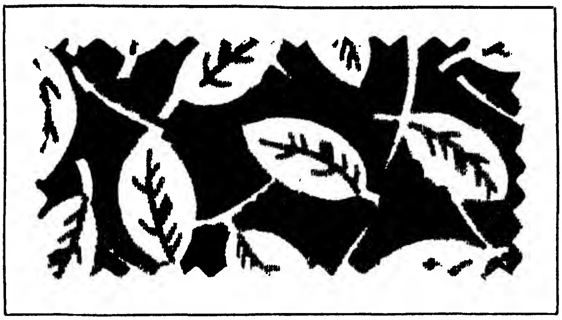
Rapidogen Green B.

60 grms. Rapidogen Green B.
30 grms. caustic soda 70° Tw.
30 grms. Monopol Brilliant Oil.
150 grms. lukewarm water.
50 grms. Glyecine A.
500 grms. neutral starch - tragacanth paste.
50 grms. urea.
130 grms. cold water.

1000

Rapidogen Green B. (I.G.).

Light green { 1 part above. 2 parts reducing paste E.



Rapidogen Brown I.B. (I.G.).

RAPIDOGEN BROWN I.B.

Made-up as Rapidogen Orange G.

Light brown { 1 part above.
2 parts reducing paste B. or E. }

Rapidogen Scarlet R. (I.G.).
,, Blue B.

RAPIDOGEN SCARLET R.

Made-up as Rapidogen Orange G.

RAPIDOGEN BLUE B.

25	grms.	Rapidogen Blue B.
30	,,	caustic soda 70° Tw.
30	,,	methylated spirit.
150	,,	lukewarm water.
30	,,	Glyecine A.
500	,,	neutral starch-tragacanth paste.
50	,,	urea.
185	,,	cold water.
1000		

The foregoing colours, printed on unprepared cloth, were developed by the acid-steaming process. After printing and drying, the goods were steamed in a rapid ager for 5 minutes in acetic-formic acid vapour and steam at 212° F., then washed, soaped at the boil, washed, and dried.

If desired the colours may also be developed by either of the two following methods:—

(*a*) *Wet Developing Process.*—The printed and dried goods are passed, without previous steaming, through a hot bath of—

20 c.c.	acetic acid 12° Tw.	per litre,
5 ,,	formic acid 90 per cent.	
25 grms.	Glauber's salt	

at 205° F. for 20 seconds, then washed, soaped at the boil, washed, and dried.

(*b*) *Drying Cylinder Developing Process.*—After printing and drying, the *unsteamed* goods are padded *on the face side* in a two-bowl mangle—the lower bowl of which is wrapped and runs in the acid—with a *cold* solution of—

30 c.c.	acetic acid 12° Tw.	per litre,
30 ,,	formic acid 85 per cent.	
40 grms.	Glauber's salt (optional),	

then dried at once on the heated cylinders of a drying machine with the *back of the cloth only* in contact with the cylinders, the first two of which must be wrapped with calico as a precautionary measure against staining the goods. The combined action of heat and the acids brings about the complete development of the printed colours, during the drying operation, and the goods, afterwards, require only to be washed and soaped in the usual way.

Rapidogen dyestuffs may be printed in multicolour styles along with Vat, Chrome, and Basic colours, Aniline black, etc., according to the methods given for Rapid Fast colours in similar circumstances. After steaming they are developed by the wet process, with the necessary additions of tartar emetic or bichromate of soda for Basic colours or for Vat colours and Aniline black respectively. The printing of Rapidogens in association with Indigosols has already been described (see Indigosols).

The Rapid Fast and Rapidogen dyestuffs enter largely into the production of many mixed and combined styles of printing—the so-called "fancy styles," which comprise discharge and resist effects on dyed and padded grounds, resists under-printed cover patterns, conversion effects, etc., the more important types of which will be described and illustrated in the following section on "Discharge and Resist Styles."

Rapidazol Colours.—Up to the present this group consists of two colours only, viz. Rapidazol Blue I.B. and Rapidazol Black B. Both are stable dyestuffs in powder form and, as they may be used in combination with Rapid Fast and Rapidogen colours, they constitute valuable additions to these two groups, neither of which includes a homogeneous black or a bright blue of good fastness to light.

Rapidazol Blue I.B. yields a full greenish-blue of excellent fastness to washing and boiling, very good fastness to light and fairly good fastness to chlorine.

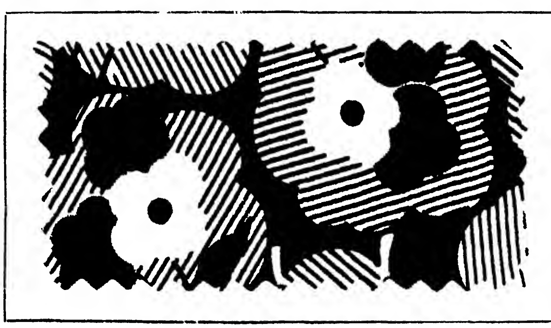
Rapidazol Black B. produces a full deep black of very good fastness to washing and boiling, of fair fastness to light and of good fastness to chlorine.

The printing colours, which are of good stability, are made-up in a similar way to those of the Rapid Fast and Rapidogen colours, viz. by dissolving the dyestuff in caustic soda and Monopol Oil or Glyecine A. (or Fibrit D.), an addition of a small proportion of chromate of soda being made for the purpose of counteracting the deteriorating influence of steam during the developing operation.

The characteristic feature which distinguishes the Rapidazol colours from

those of the Rapid Fast and Rapidogen groups is, that in developing the prints, the formation of the actual colouring matter, on the fibre, can *only* be brought about by means of steam—*an ordinary steaming* (*without acid*) *in a rapid ager*—and *not at all* by the hot acid processes essential for other Azoic combinations. Once steamed, however, the Rapidazol colours are immune to acid treatments; consequently, when printed in combination with Rapid Fast or Rapidogen dyestuffs, the printed goods are first steamed to develop the Rapidazol colours and then, subsequently, put through the acid processes appropriate to the development of the other colours. When printed along with Vat colours, a single passage through the rapid ager suffices for both.

The method of developing Rapidazol colours by steaming suggests an analogy between these colours and the Steam Para reds of Fourneaux (*q.v.*) and Keilmann, which consist essentially of mixtures of nitrosamines with 2-naphthol-1-sulphonic acid and 2-naphthol-1-carboxylic acid respectively. There is a difference, however; in the two reds mentioned, the sulphonic and carboxylic groups are split-off from the *naphthol* component on steaming, giving free β-naphthol, which couples up at once with the diazo-compound, whereas in the case of the Rapidazols, which are mixtures of stable diazo-compounds with naphtholates, this type of reaction cannot occur, and, therefore, any splitting-off of acid must be from the *diazo*-component, giving a free diazo-compound which couples with the naphtholate present. No exact information as to the actual composition of the Rapidazol colours has been made public, but from the facts that the blue yields Variamine blue on steaming, and that the nitrosamine of Variamine blue is not easy to make, it may be surmised that the difficulty of preparing a Rapid Fast or Rapidogen Variamine blue has been overcome by making a specially stable salt of its diazo-compound and combining this with Naphthol A.S. Such a salt as the diazo-sodium sulphonate of 4-ethoxy-4′-aminodiphenylamine when mixed with Naphthol A.S. in caustic solution yields Variamine blue on steaming. Similarly the tetrazo-sodium sulphonate of di-*p*-aminodiphenylamine gives a black; in both cases sulphur dioxide splits-off in steaming and coupling takes place. In all probability the Rapidazol colours possess a similar chemical structure. Be that as it may, the Rapidazols are exceedingly useful colours; their simple method of development and fixation by steaming alone places them in the class of steam colours, and enables them to be used along with certain other colours which are susceptible to acid treatments and, therefore, cannot be employed with Rapid Fast and Rapidogen dyestuffs; they also supplement the ranges of the latter dyestuffs by rendering available for use along with them two valuable bases which previously could be printed only on naphthol-prepared cloth.



Dark Blue: Rapidazol Blue I.B., 5 per cent.
Light Blue: „ „ „ 1·25 per cent.
Red: Rapid Fast Scarlet R.H. powder, 7 per cent. (see Rapid Fast colours). (I.G.).

Rapidazol Blue I.B. and Rapidazol Black B. are, at present, the only examples of practicable and satisfactory steam-developed Azoic colours in current use; but it is not unlikely that, in the near future, the principles of

their preparation will be applied to other colour bases and, in view of their simple method of fixation, it is probable that, other things being equal, the Rapidazol type of colour will eventually displace those types at present employed for printing on unprepared fabrics.

PRINTING COLOURS (pattern on previous page).

Red.

Made up on the lines of Rapid Fast Orange R.H. (*q.v.*).

Dark Blue.

50	grms.	Rapidazol Blue I.B.
20	,,	Glyecine A.
20	,,	caustic soda 70° Tw.
395	,,	cold water.

Mix to a fine paste, allow to dissolve, and add to—

500	grms.	neutral starch-tragacanth paste.
15	,,	neutral chromate solution.
1000		

Light blue.

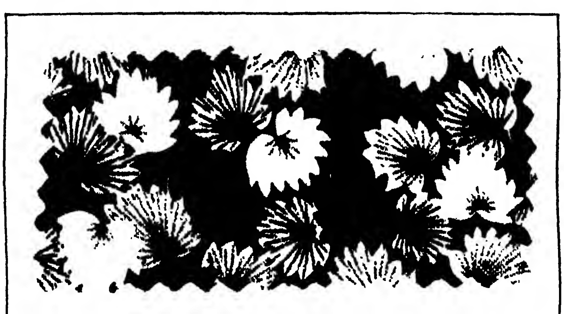
1 part Dark blue.
3 parts reducing paste, below.

REDUCING PASTE.

500	grms.	starch-tragacanth paste.
5	,,	caustic soda 70° Tw.
15	,,	neutral chromate solution.
480	,,	water.
1000		

Print, dry, and steam the goods for about 10 minutes with saturated steam in the rapid ager to develop the Rapidazol blue; then develop the Rapid Fast scarlet in the usual manner by slop-padding through a hot solution of 30 c.c. acetic acid and 50 grms. Glauber's salt per litre (temperature 160°–175° F., time of immersion ½–1 minute), wash, soap at the boil, and dry. The Rapid Fast scarlet may also be developed by steaming a second time in the presence of acetic acid.

If Rapidogen colours are printed with either of the Rapidazols, the foregoing process is slightly modified to conform to the usual Rapidogen developing processes.



Red: Rapidogen Scarlet R., 8 per cent.
Black: Rapidazol Black B., 8 per cent. (I.G.).

Printing Colours.

Red.

For recipe, see Rapidogen Colours.

Black.

80	grms.	Rapidazol Black B.
30	,,	Glycecine A.
30	,,	caustic soda 70° Tw.
390	,,	cold water.
450	,,	neutral starch-tragacanth paste.
20	,,	neutral chromate solution.
1000		

Print, dry, and steam for about 10 minutes as before. The Rapidogen colour is then developed by any of the methods already described, viz. (*a*) the wet developing, (*b*) the drying cylinder developing, (*c*) the acid-steaming developing process.

Useful grey shades may be produced by reducing the colour content of the foregoing printing black, or simply by adding any desired quantity of the reducing paste given for Rapidazol Blue I.B.

The printing of Rapidazol colours along with supplementary colours of the Vat, Chrome, and Basic colour groups presents no variation from the normal processes employed in the printing of those dyestuffs. Such mixed colourings are not in great demand, but occasionally they are convenient and sometimes are useful for obtaining special effects.

The Azoic colours, in general, whether printed or padded in the form of diazo solutions or of Rapid Fast, Rapidogen, or Rapidazol colours, are applicable to all vegetable fibres and artificial silks, and to fabrics consisting of mixtures of these fibres. On acetyl silks (Celanese, etc.), the alkaline Rapid Fast and Rapidogen colours give excellent results, and they provide a useful means of applying Azoic colours to these somewhat unaccommodating materials.

(4) DISCHARGE AND (5) RESERVE (RESIST) STYLES.

Perhaps the most important of the many valuable features of Discharge and Reserve or Resist styles of printing is that they allow of white and coloured patterns being produced on *dyed* grounds.

As is well known, it is possible to obtain by dyeing a depth, fullness, and richness of colour altogether unapproachable by any process of printing. It is a very great advantage, therefore, to be able to print upon white cloth a reserving or resisting substance which will prevent the fixation of colour during the dyeing operation; or to print upon dyed cloth a substance which will discharge the colour from the printed parts. But these styles are not restricted to dyed work; they may be, and are, applied equally well to all sorts of printed patterns, so that it is possible to obtain a vast variety of effects on figured backgrounds. Any colour that can be dyed and printed can be discharged or reserved, irrespective of the method by which it has been applied, provided always that it is suited to this class of work. Mordants can also be treated in the same way, as has already been noted in the description of the Madder style.

Another advantage, which relates more particularly to discharge printing, is that fine, delicate patterns can be discharged on dark grounds with a per-

fection and crispness of definition quite impossible in printing with a blotch roller. In the latter case, the colour always runs to a slight extent, and this, with delicate line or spot patterns, is almost invariably sufficient to spoil the sharpness of the impression; the colour swells, and fills up the finer details of the design. Some improvement may be effected in the impression of a blotch roller by using thicker colour, but then the ground colour suffers, and is very apt to become thin and weak in appearance, or " clothy " or " bare " as it is termed technically. On the whole, therefore, it is safer and better in all respects to employ the discharge or the resist methods whenever circumstances permit.

Discharging agents always act chemically. Resisting or Reserving agents may act either chemically or mechanically ; very often they do both. It is needless to give a detailed list of the numerous substances that go to make up the various discharges and resists ; but it may be noted that both classes of bodies include oxidising and reducing agents, acids and alkalies, various salts, China clay, and, in the case of resists, fats, wax, resin, and solid matter like lead or barium sulphate.

The chemical action of these substances will be touched upon here only in so far as it relates to their suitability for producing patterns on dyed and printed grounds ; but further information on the nature and properties of oxidising and reducing agents will be found in the special chapter on these bodies.

DISCHARGE STYLES.

The Discharging of Indigo by Oxidation.

Indigo may be discharged either by oxidising or reducing agents. Processes based on oxidation were for a long period the only means available for obtaining discharged patterns on a dyed Indigo ground and, although they have lost much of their former importance, they are still in current use. Except in fine patterns, oxidation discharges are liable to attack and weaken the cotton fibre and, for this reason, they are now replaced, wherever possible, by newer *reduction* processes which are free from this disadvantage. Nevertheless, oxidation discharges are yet of considerable importance and for certain classes of work they are indispensable.

Oxidising agents convert Indigo into isatin, which dissolves out of the cloth during the process, leaving a white pattern wherever the cloth was printed. The most important substances used for this purpose are—(1) Chromates ; (2) Bromates ; (3) Chlorates ; (4) Red prussiate of potash in combination with caustic soda ; and (5) Nitrates and Nitrites. The methods depending on the use of these reagents are distinguished as—

(1) The Chromate Discharge.
(2) The Bromate Discharge.
(3) The Chlorate Discharge.
(4) The Prussiate Discharge.
(5) The Nitrate Discharge (Freiberger).

Each possesses certain advantages in special cases, but the first is by far the most generally useful and finds the most extensive application.

(1) The Chromate Discharge.

In this process the Indigo-dyed cloth, printed with a pattern in a chromate, is passed through a hot bath of sulphuric and oxalic acids ; chromic acid is liberated and destroys the Indigo. At the same time, however, the cloth is

liable to be tendered by the formation of oxycellulose, especially if an excess of chromate be used in the discharge. Under the most favourable conditions a slight tendering always takes place, as it is impossible to gauge exactly the quantity of chromate required for a given shade of blue; and if too little is taken, the white is poor. Hence it is advisable to use a small excess of chromate in order to obtain a clear, sparkling white. To some extent the formation of oxycellulose can be regulated by the addition of reducing agents to the acid or cutting liquor; the addition of glucose, glycerine, brown sugar, and dextrin has been recommended for this purpose, but hitherto they do not seem to have exercised any particularly beneficial effect. Oxalic acid acts in much the same way, and is perhaps the best, as it is certainly the most commonly used, substance to counteract the energetic oxidising action of chromic acid. It tends to regulate the discharging, and simultaneously it renders the excess of chromic acid in the bath innocuous by reason of its neutralising properties. If the chromic acid were allowed to accumulate, it would soon become sufficiently concentrated to affect the colour on the unprinted parts of the cloth; indeed, with light Indigos it not infrequently happens that the colour is partially destroyed over the whole surface of the cloth, owing to an excess of chromic acid in the cutting liquor.

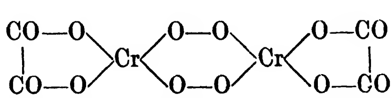
It is generally supposed that the function of oxalic acid, in the mixed cutting bath of sulphuric and oxalic acids, is solely to neutralise, *by reduction*, the stripping action of any excess of chromic acid that may accumulate in the bath during the course of continuous working. Such, however, is by no means the whole of the case; for, sulphuric acid alone will not give a satisfactory result as regards cutting, whereas oxalic acid alone gives perfect whites. Hence oxalic acid cannot be regarded, purely and simply, as a reducing agent.

The reactions which take place in the Chromate-discharge process are not so simple as those usually given in textbooks. Quite otherwise; for not only is the function of oxalic acid totally different, but the reactions are somewhat complex. According to Schaposchnikoff and Michireff (*Zeits. Farben-u-Textile Chem.*, 1902) the reactions take place in two stages or phases—the first, between the chromate and sulphuric acid, resulting in chromic acid and potassium or sodium sulphate; the second, between the chromic acid and oxalic acid giving chromium hydrate, carbon dioxide, and *free oxygen.*

(1) $Na_2CrO_4 + H_2SO_4 = Na_2SO_4 + CrO_3 + H_2O$
(2) $2CrO_3 + C_2H_2O_4 + 2H_2O = 2CO_2 + 2Cr(OH)_3 + O_2$

The liberated oxygen immediately oxidises and destroys the Indigo, and the chromium hydrate is dissolved by the excess of sulphuric acid present. Thus it would appear that oxalic acid, so far from playing the rôle of reducing agent, popularly assigned to it, does exactly the reverse so far as Indigo is concerned—it assists in the oxidation.

This view is confirmed by Prud'homme,[1] who showed that, during the oxidation of oxalic acid by chromic acid, ozone is formed. Chromic and oxalic acids condense to form an unstable compound of the following constitution:—

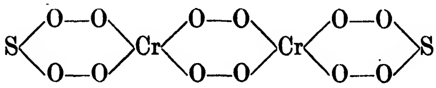


which, when acted upon by a further amount of oxalic acid, splits up as under:—

$$Cr_2C_4O_{12} + H_2C_2O_4 = Cr_2(C_2O_4)_3 + H_2O + O_3$$

[1] *Révue générale des matières colorantes*, 1903.

With sulphuric acid a similar but more stable compound is formed—



which does *not* yield ozone on treatment with excess of acid. If, however, Indigo be added (as, for example, a piece of Indigo-dyed cloth) partial reduction takes place, ozone is formed, and the Indigo is more or less destroyed. On the other hand, the compound is decomposed by alkalies and ozone is produced :

$$2Cr_2S_2O_{12} + 12NaOH = 2Cr(OH)_3 + 2Na_2CrO_4 + 4Na_2SO_4 + 3H_2O + O_3$$

The above formulæ and equations demonstrate that the reduction of chromium salts by oxalic acid involves more than is commonly attributed to the operation, and that, under suitable conditions, the usual reducing action of oxalic acid may be reversed. In passing it may be noted that the question of the reduction of chromic acid and its salts is of great interest, inasmuch as it presents other variations from generally accepted theory.

One of the most important advantages of the Chromate discharge is that it allows of bright and fast colour effects being obtained on an Indigo-blue ground of any depth. The pigment colours—Chrome yellow, Chrome orange, Guignet's green, Yellow ochre, Sienna, Lampblack, Vermilion, and various lakes and Prussian blue—are used for this purpose. They are fixed with albumen, which is coagulated during the run through the acid bath. Steaming is both impossible and unnecessary, the hot acid effecting the coagulation quite as well, and in a manner sufficiently complete to fix the pigments permanently.

For a discharge white, the bichromates of soda and potash may be used as such ; they are simply dissolved in water and added to starch paste or British gum thickening. For colours, however, they must be neutralised with caustic soda, soda-ash, or ammonia, otherwise the acidity of the bichromates would coagulate the albumen before the colour was printed. Excess of ammonia is not detrimental, except to colours containing Prussian blue ; and in the case of Chrome yellows, and the various oxides of iron, and the earths, an excess of soda-ash even may be allowed. A little free alkali improves the working qualities of printing colours containing albumen, but care should be taken not to add too much, lest the coagulation be retarded.

The general directions, given elsewhere (Preparation of Printing Colours), for the grinding and straining of pigment colours must be strictly followed in discharge printing if good results are to be secured. A brush furnisher must also be used ; and it is advisable at the outset to add a little turpentine, benzene, or oil to the printing colours to prevent any undue frothing.

The percentage of bichromate in the printing pastes varies with the depth of the Indigo blue to be discharged, and with the strength of the engraving. Coloured discharges usually require less than white discharges, as the opaque pigments mask the slight under-tint of blue.

The following examples of Chromate discharges are taken from practice :—

White 160 I.

810	grms.	British gum paste.
160	,,	bichromate of soda.
30	,,	turpentine.
1000		

YELLOW 120 I.

320	grms.	Chrome yellow.
60	,,	6 per cent. tragacanth thickening.
20	,,	rape seed oil.
20	,,	turpentine.
300	,,	40 per cent. albumen solution.
120	,,	bichromate of soda.
100	,,	caustic soda 70°-71° Tw.
60	,,	water.
1000		

GREY 120 I.

250	grms.	Lampblack.
280	,,	6 per cent. tragacanth thickening.
200	,,	40 per cent. albumen.
120	,,	bichromate of soda.
50	,,	water.
100	,,	caustic soda 70° Tw.
1000		

GREEN 120 I.

200	grms.	Guignet's green.
100	,,	Chrome lemon yellow.
100	,,	6 per cent. tragacanth thickening.
300	,,	40 per cent. albumen.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
50	,,	water.
30	,,	turpentine.
1000		

STRAW 120 I.

300	grms.	Chrome yellow.
10	,,	Prussian blue 25 per cent.
70	,,	6 per cent. tragacanth thickening.
300	,,	40 per cent. albumen.
40	,,	rape seed oil.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
60	,,	water.
1000		

RED 90 I.

200	grms.	Vermilion. } or 300 grms. Limol red[1] 50 per cent. paste.
100	,,	Vermilion substitute }
140	,,	6 per cent. tragacanth thickening.
90	,,	bichromate of soda. Grind together, and add in turn—
145	,,	6 per cent. ammonia.
20	,,	rape seed oil.
30	,,	turpentine.
275	,,	50 per cent. egg albumen.
1000		

[1] Limol red gives a fine and fast colour.

BROWN 120 I.

250	grms.	Burnt Sienna paste.
100	,,	6 per cent. tragacanth thickening.
300	,,	40 per cent. albumen.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
90	,,	water.
40	,,	rape seed oil.
1000		

CHAMOIS 120 I.

60	grms.	Chrome yellow (lemon).
20	,,	,, ,, (maize).
150	,,	China clay.
150	,,	water.
300	,,	6 per cent. tragacanth thickening.
100	,,	50 per cent. egg albumen.
120	,,	bichromate of soda.
100	,,	caustic soda 70° Tw.
1000		

Various shades of olive can be obtained by mixing yellow, green, and grey, or from some of the many colour lakes of all descriptions put on the market for discharge styles by different makers.

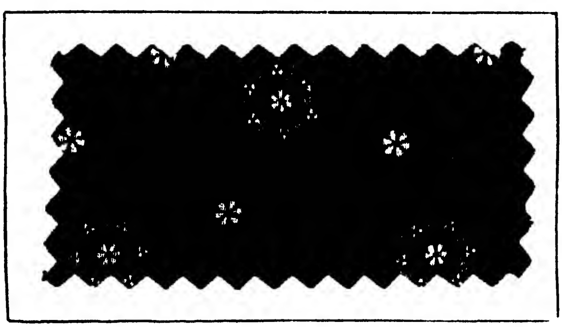
The numbers in the foregoing recipes denote the amount of bichromate per kilogramme of colour, and those given are suitable for the ordinary dark shade of Indigo blue.

After printing the above colours, the Indigo-dyed cloth is dried and then passed through the following bath at 60° C.:—

ACID OR CUTTING BATH.

60	grms.	sulphuric acid 168° Tw.
20–30	,,	oxalic acid.
920–910	,,	water.
1000		

The speed of the cloth is arranged so that it takes about $\frac{1}{2}$ minute to pass through the acid bath; that is, the time of immersion is $\frac{1}{2}$ minute. From time to time the bath is replenished by the addition of fresh liquor. The goods are finally well washed and dried.



Discharge White and Yellow on Indigo (Chromate) (C.P.A.).

The concentration of the cutting liquor varies in different works: the above has been found to give excellent results on the large scale, but the proportions of the two acids may be varied considerably without appreciably affecting the ultimate effect.

A modification of the Chromate discharge, first suggested by Prud'homme, and later worked out by others, was, formerly, largely used in Russia and, to some extent, also in England. It consists in dispensing with oxalic acid in the cutting liquor, and adding oxalate of potassium or of calcium to the printing colour. Good results are said to be obtained with both white and colours, and it is claimed for the process that it effects a considerable economy in oxalic acid. This is not unlikely, but the process has not been shown to possess any conspicuous advantage over the older one, and has not come into general use.

CHROMATE DISCHARGE WHITE WITH OXALATE.

180	grms.	bichromate of soda.
80	,,	20 per cent. ammonia.
540	,,	British gum paste.
200	,,	calcium oxalate 50 per cent. paste.
1000		

Print on dark Indigo, dry, and discharge in—

80	grms.	sulphuric acid 168° Tw.	at 60° C.
920	,,	water	
1000			

Wash well and dry.

Cheap dark shades of blue are obtained by first dyeing the cloth a light Indigo blue and then padding it in a weak Aniline black bath. The same principle is applied differently in the production of discharge effects on a two-colour ground of Indigo blue and Aniline black. The light blue goods are printed in Chromate discharges containing acetate of soda, or better, an excess of soda-ash; they are then covered with a pattern in Aniline black, dried, passed through the rapid ager to develop the black, and finally cut, as described above, in sulphuric and oxalic acids. The presence of free alkali prevents the development of the black on the printed parts, so that a clear-cut pattern in discharge colours appears on a blue and black ground. Some of the styles produced in this way are very effective, and they had a great run some years ago.

The following two colours will illustrate the preparation of Chromate discharges to resist a black cover or pad:—

CHROMATE WHITE TO RESIST BLACK COVER.

60	grms.	bichromate of soda.
150	,,	soda-ash.
200	,,	water.
590	,,	British gum paste.
1000		

YELLOW TO RESIST BLACK COVER.

40	grms.	bichromate of soda.
100	,,	soda-ash.
100	,,	British gum.
10	,,	olive oil.

Heat until the gum is dissolved, then cool and grind in—

260	grms.	Chrome yellow (paste).
160	,,	40 per cent. albumen.
Water to 1000		

Print on light Indigo-dyed cloth; dry; cover in a prussiate Aniline black, pass through the rapid ager, discharge in acid, wash well, and dry. A red may be obtained by replacing Chrome yellows with Vermilion, or one of the Vermilion substitutes.

Conversion Effects with Indigo.—In combination with other vat dyestuffs Indigo is capable of yielding a variety of colours and effects. With Indanthrene and similar yellows it forms an olive green very fast to light and soap. Indanthrene yellow is not destroyed by oxidising agents, so that if a pattern printed with the mixture is over-printed with another pattern, in bichromate of potash, and passed through a cutting-bath of sulphuric and oxalic acids, the Indigo component is destroyed, where the bichromate is printed, leaving a bright yellow, and thus producing a green and yellow conversion effect.

If the green be printed on cloth dyed a light shade of Indigo, and then treated as above, the result is a four-colour effect from two rollers only, viz. green, yellow, light blue (the ground colour), and white (a portion of the ground colour discharged). Durindone red 3 B., Caledon jade green, and many dyestuffs of the Caledon and Indanthrene series, may be applied in like manner, either with Indigo alone or in various mixtures along with Indigo. According to the colours used the conversion colours will be crimson, light blue, green, violet, or brown. If a chlorate discharge is printed similar results are obtained; and by using a chlorate discharge containing a lead salt the final shades are considerably modified when the goods are subsequently chromed to convert the lead salt into lead chromate.

Azoic Colour Discharges on Indigo.—The fact that certain diazo compounds withstand the action of chromic acid has been utilised for the production of red and orange discharges on Indigo. For this purpose the most suitable amino bases to use are aminoazo-benzene, *p*-nitraniline, and *m*-nitraniline; most of the others are more or less acted upon by chromic acid, and some of them are entirely destroyed.

The discharge colours are made up as usual for Azoic colours plus the required amount of bichromate of soda, and are then printed on Indigo-dyed cloth prepared in β-naphtholate of soda. After drying, the printed goods are discharged by running through the acid cutting bath, as used for Indigo, at a temperature of 50°-60° C. They are then well washed and dried.

Discharge Red or Orange.

	Red.	Orange.
Paranitraniline	22 grms.	..
Metanitraniline	..	22 grms.
Water	200 c.c.	200 c.c.
Hydrochloric acid 36° Tw.	33 „	33 „
Ice and water	100 „	100 „
Nitrite of soda 29 per cent. solution	39 „	39 „
Filter and add:—		
Gum-tragacanth thickening 6 per cent.	400 c.c.	400 c.c.
Bichromate of soda	150 grms.	150 grms.
Sodium acetate	75 „	75 „
Make up to	1 litre.	

Print on Indigo-blue cloth previously padded in naphthol prepare 1, 2, 3, 4, or 5 (p. 510); dry, and pass through the ordinary cutting liquor; wash well and dry.

The insoluble Azoic colours can be printed along with all the ordinary chromate discharges except white, which is difficult to obtain pure, as the chromic acid acts on β-naphthol, producing a dirty brownish coloration. The only way of overcoming this disadvantage is to wash the goods free from naphthol before they are passed into the acid bath. With soluble chromates this is impossible, so that insoluble chromates have to be used. These are either produced upon the fibre directly or added to the printing colour in paste form.

Kurz and Kunert have worked out a method based upon the employment of a naphthol prepare containing sodium bichromate, and printing colours containing lead acetate. Chromate of lead is deposited on the fibre, and the goods are then rinsed in water to remove the naphthol grounding before being treated in the acid bath. The lead chromate resists the washing, and is subsequently decomposed with the liberation of chromic acid during the cutting operation. To avoid the deposition of lead sulphate on the cloth, the cutting liquor may be composed of hydrochloric and oxalic acids in place of the usual sulphuric acid liquor.

Messrs Meister, Lucius & Brüning recommend the addition of barium chromate to the diazo discharge colours, which can then be printed on naphtholate of soda prepares, pure and simple. Thus—

Barium Chromate Discharge Red.

350	c.c.	diazo-solution from 22 grms. *p*-nitraniline.
{300	grms.	thick tragacanth mucilage 8 per cent.
{300	,,	barium chromate 85 per cent. paste.
50	,,	sodium acetate.

To 1 litre.

Print on naphthol-prepared Indigo-dyed cloth; dry, and then pass in the open width through dilute ammonia to remove the superfluous naphthol: squeeze out the excess of ammonia, and pass through a cutting liquor composed of 60 parts hydrochloric acid at 33° Tw. and 20 parts oxalic acid per 1000 of water; wash well, soap, and dry. The washing in dilute ammonia previous to cutting requires the greatest care, otherwise a portion of the mechanically adhering barium chromate will be detached, with the result that the Indigo will be incompletely discharged.

Although the diazo compounds of the para- and meta-nitranilines and aminoazo-benzene all resist the action of chromic acid sufficiently long to allow of their being utilised for coloured discharges, they are, nevertheless, slowly acted upon by it, and therefore it is advisable to prepare the colours in small quantities as required. The sodium bichromate ought to be added immediately before printing, and the colour ought to be printed at once. Even then it is difficult to obtain regular results if the colour is not renewed at frequent intervals. On the whole, the Azoic colour discharge style on Indigo is somewhat unreliable, and for that reason it finds but little application in practice.

(2) The Bromate Discharge.

Another method of discharging Indigo may be noted here, as it bears a close resemblance, in some respects, to the Chromate process. It was worked out

and patented by Dydynksi and the Calico Printers' Association in 1906, and is based upon the oxidising action of bromine. The process consists in printing the Indigo-dyed calico with a mixture of bromide and bromate of sodium, and then in passing the goods through a cutting liquor of dilute sulphuric acid (12 per cent.) at 85°–93° C. The liberated bromine oxidises the indigotine to isatin, producing a white discharge.

$$5NaBr + NaBrO_3 + 3H_2SO_4 = 3Na_2SO_4 + 3H_2O + 3Br_2$$

In practice, an excess of bromate is found to yield better results. Instead of the 22·7 per cent. of bromate in the mixture, it is better to employ a quantity between 25 per cent. and 30 per cent. The cutting liquor may be used at 40°–50° C., but better and cleaner discharges are obtained at the temperature mentioned above (85°–93° C.). The speed at which the cloth is run through the cutting liquor is regulated so as to allow of a 7–20 seconds' immersion, according to the class of work in hand. All chance of bromine vapour escaping into the air is avoided by adding a little ferrous sulphate to the cutting liquor. Most of the bromine accumulates in the bath as sodium bromide, and may be recovered from the cutting liquor by distillation with bichromate of soda and acid.

For discharging a dark shade of Indigo the following is a suitable paste for a fairly fine pattern :—

WHITE DISCHARGE B.R.

180 grms. bromate of soda.
420 ,, bromide ,,
1 litre British gum paste.

Print, dry, pass through 12 per cent. sulphuric acid at 85°–90° C. ; wash well and dry.

(3) The Chlorate Discharge.

This process is chiefly used for the production of white effects only, since it cannot be applied along with colours which are comparable with Indigo for fastness, and at the same time as bright as those obtained by the Chromate method. In some cases, however, Chlorate discharges are combined with pigment colours, but goods so printed cannot afterwards be passed through caustic soda, in order to improve the white.

The Indigo is discharged by steaming in the rapid ager for 1–3 minutes, and the discharge printing pastes contain, besides chlorate of soda, a certain amount of red or yellow prussiate of potash or vanadium salts, both of which act as oxygen carriers. The addition of citric acid or citrates of soda or ammonia also improves the discharge, but care should be taken to avoid an excess of acid, as the fibre is easily tendered thereby. For fine patterns which require a more energetic oxidising agent to discharge the Indigo properly, chlorate of soda is replaced by chlorate of alumina. The chief defect of chlorate discharges is, that they are liable to run in steaming. To minimise this, it is usual to add a plastic substance, like China clay, to the printing pastes, and to steam the goods in dry steam as hot as possible.

Chlorate discharges are especially suitable for heavy patterns, since they are less apt to form oxycellulose than chromate discharges ; and for very heavy patterns their oxidising action is often still further moderated by replacing part of the chlorate with bromate of soda or ammonia. Bromine and its oxy-acids do not attack the fibre so energetically as chlorine and its oxides.

To obtain a good white on Indigo, the dyed cloth must be well soured and

washed after dyeing in order to remove all traces of lime or alkali. If these are allowed to remain, the discharge will be irregular and the white poor. The rollers, too, must be strongly engraved, so that the discharge may be effected completely in one steaming operation of from 1 to 3 minutes; a longer steaming increases the risk of running.

To prevent doctor streaks from discharging the blue ground where not required, the cloth may be prepared before printing in dilute solutions of sulphites, thiosulphites, or sulphocyanides. These salts act as effective resists to the action of the small quantity of chlorate transferred to the cloth through a defective doctor, but do not, at the strength used, affect to any appreciable extent the discharge of the Indigo in the properly printed parts.

The following chlorate discharges are suitable for dark shades of Indigo; lighter shades require reducing according to their intensity.

CHLORATE DISCHARGE WHITE I. 20 per cent.

250 grms. British gum powder.
470 ,, water.
200 ,, chlorate of soda.

Boil, cool to 30° C., and add—

50 grms. yellow prussiate of potash (finely ground) and
30 ,, citrate of ammonia 50° Tw.

1000

CHLORATE WHITE II. 15 per cent.

A { 50 grms. starch.
250 ,, water.
200 ,, 50 per cent. China clay paste.
150 ,, chlorate of soda. Boil and cool. }

B { 30 ,, yellow prussiate of potash.
245 ,, 6 per cent. tragacanth thickening.
75 ,, citric acid (powder). }

1000

Mix A and B.

CHLORATE WHITE III. 15 per cent.

80 grms. China clay.
75 ,, water.
530 ,, 40–50 per cent. gum Senegal.
150 ,, chlorate of soda. Dissolve, cool to 30° C., and add—
90 ,, tartaric acid in powder. Cool, and add—
75 ,, ammonium ferricyanide 36° Tw.

1000

CHLORATE WHITE IV. 20 per cent.

250 grms. British gum powder.
400 ,, water.
100 ,, 50 per cent. China clay paste.
200 ,, chlorate of soda. Dissolve, cool to 30° C., and add—
20 ,, red prussiate of potash (ground). Cool, and add—
20 ,, ground citric acid.
10 ,, vanadium solution 1 per cent. (see Mordants).

1000

Aluminium Chlorate White I.

200	grms.	British gum powder.
60	,,	water.
550	,,	chlorate of alumina 42° Tw.
150	,,	chlorate of soda. Boil, cool, and add—
40	,,	red prussiate of potash.
1000		

Aluminium Chlorate White II.

45	grms.	flour.
250	,,	water.
150	,,	chlorate of soda.
200	,,	,, barium. Boil, cool to 50° C., and add—
130	,,	sulphate of alumina.
130	,,	boiling water. Cool, and add—
40	,,	red prussiate of potash (powder).
55	,,	8 per cent. tragacanth thickening.
1000		

Chlorate Discharge Yellow A.

250	grms.	Chrome yellow paste.	Grind well together in a mill and add—
200	,,	40 per cent. albumen.	
150	,,	chlorate of soda.	
280	,,	8 per cent. tragacanth thickening.	
30	,,	red prussiate of potash (ground).	
50	,,	citrate of soda 40° Tw. (neutral).	
20	,,	olive oil.	
20	,,	turpentine.	
1000			

All the foregoing chlorate discharges are printed on cloth dyed dark Indigo. After printing, the goods are dried and steamed for 1–3 minutes in the rapid ager with dry steam at 95°–100° C. ; then washed in water for 2–4 minutes at 60°–80° C., and, if they contain no yellow, passed in the open width through caustic soda at 4° Tw., or through a bath composed of equal parts of caustic soda and silicate of soda made up as under:—

10	litres	caustic soda 66° Tw.
10	,,	silicate of soda 66° Tw.
1000	,,	water.

If the pattern contains yellow, the goods are simply washed and lightly soaped after steaming.

Another method of producing a Chrome yellow discharge on Indigo is sometimes employed for certain African styles. The yellow is produced on the fibre after the discharging has been effected by the chlorate. For this purpose the following paste is printed on a medium shade of indigo:—

Chlorate Discharge Yellow B.

450	grms.	water.
155	,,	British gum.
100	,,	chlorate of soda.
175	,,	lead nitrate. Dissolve with heat, cool a little, and add—
50	,,	citric acid. Cool, and add—
20	,,	red prussiate of potash.
50	,,	water.

Print; steam 3 minutes; pass through a hot solution of sulphate of soda, and then directly into a hot ½ per cent. solution of bichromate of potash (neutralised with ammonia) to raise the lead yellow. A slight excess of ammonia is beneficial in giving a warmer tone to the lead chromate. Finally, wash well and dry.

The above discharge yellow is principally used in the production of the bizarre mixed-up effects so popular in the West Coast of Africa trade. An example of these curious effects is produced by the following series of operations:—

On white cloth prepared in oleine 2½–4 per cent.

(1) Print a stripe pattern (or any other) in Alizarin red and pink, Pigment yellow, Pigment green. Steam and wash.

(2) Dip the printed goods to a medium shade of Indigo, corresponding to, say, about 1 per cent. of Indigo on the cloth. Wash well in water and soap lightly.

(3) Print a two-colour scroll pattern in Chlorate white III. reduced to 10 per cent. and Chlorate discharge yellow B. Steam for 3 minutes in the rapid ager; wash off in sulphate of soda; wash well in water; develop the Chrome yellow by a run through a 1 per cent. solution of neutral chromate of soda at 60° C.; wash well again and soap lightly to clear the white and colours.

The ultimate result is a scroll pattern in white, yellow, red, pink, scarlet, orange, and two shades of green, on a striped ground of pure Indigo blue, a purplish shade of blue, a greenish blue, a chocolate, and a green. The chlorate discharges cut away the Indigo, allowing the pattern first printed to show through, and the shades of orange, scarlet, and yellowish green are obtained from the superposition of the discharge yellow on red, pink, and green. The strength of the discharges is arranged so that they cut the Indigo without affecting the colours underneath it; and care must be taken to avoid using them at a greater strength than is necessary for this purpose, as if too strong they will discharge, or at least partially discharge, the steam Alizarin pink and reduce the depth of the Alizarin red. The parti-coloured ground is, of course, the result of dyeing Indigo over the pattern first printed.

Various other motley effects of a similar nature are obtained by combinations of the Madder style with Indigo dyeing and chlorate discharges.

Chlorate of alumina discharges can be applied to the production of an Alizarin red discharge on Indigo. The dyed goods, after printing and steaming, are passed at once through any of the usual dunging liquors to fix the alumina, and then dyed up in Alizarin as usual for the Madder styles (F. Brandt. See also Prud'homme, *Teinture et Impression*, p. 154).

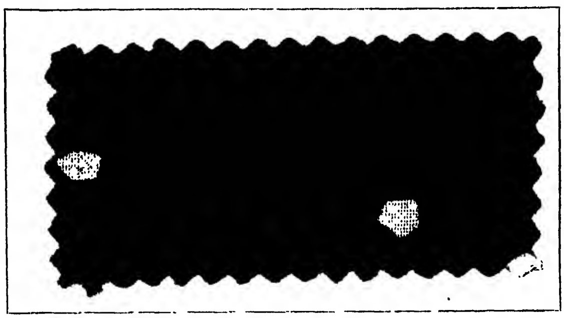
Another method of producing fast-coloured discharges on an Indigo ground is based upon the fact that certain Azoic colours are unaffected by the oxidising action of chlorate discharges. Of these colours, the best known is the red obtained from the diazo-compound of paranitro-orthoanisidine coupled with β-naphthol. The process is as follows:—The Indigo-dyed cloth is first padded in a 2½–3 per cent. β-naphthol prepare according to the methods already mentioned in connection with the production of the insoluble Azoic colours: it is then printed with the red and white discharges given below, and, after drying, steamed for 4 minutes in the rapid ager. Finally, it is worked for 10–15 minutes in a 1 per cent. solution of silicate of soda at 60° C., washed well, soaped, washed again, and dried.

	Discharge Red.	Discharge White.
{Thick flour paste	400 grms.	550 grms.
{Chlorate of soda	250 ,,	250 ,,
Dissolve, cool, and add—		
Chlorate of aluminium 42° Tw.	45 ,,	50 ,,
{Red prussiate of potash (powdered),	25 ,,	25 ,,
{Water	80 ,,	100 ,,
Cool completely and add—		
Citric acid	25 ,,	25 ,,
Acetate of soda	25 ,,	..
Diazo solution A.Z.P.	150 ,,	..
	1000	1000

Diazo Solution A.Z.P.

{168 grms. *p*-nitro-*o*-anisidine (Azo pink N.A.).
{300 grms. hydrochloric acid 36° Tw.
{300 grms. water.

Mix to a fine paste and add—
450 grms. ice water.
And then slowly—
260 grms. nitrite of soda 29 per cent. solution.
Make up to 1500 grms. with water.



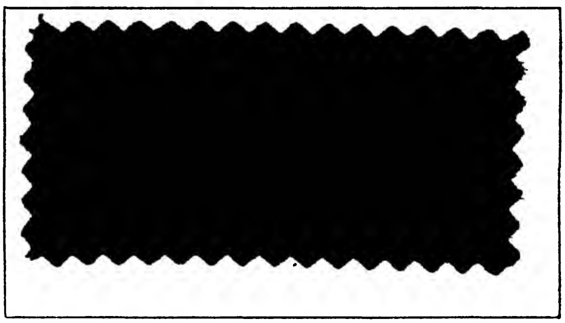
Chlorate White and Azo Pink N.A. (I.G.).

Chlorate Discharges with Naphthol A.S. Combinations on Indigo.—A greater variety of fast colour discharges is obtained on Indigo by using naphthols of the A.S. group in place of β-naphthol, and by substituting certain Fast Colour Bases or the corresponding Fast Colour Salts for *p*-nitro-*o*-anisidine. The range of coloured effects obtained in this way includes yellow, golden yellow, oranges, and all shades of reds and scarlets. The following combinations are the most suitable for this style, the working details being identical with those given for *p*-nitro-*o*-anisidine :—

For yellow :—	Naphthol A.S.-G.	/ Fast Scarlet T.R. base.
	,, A.S.-G.	/ ,, Red K.B. base.
For golden yellow :—	,, A.S.-G.	/ ,, Orange G.R. base.
For orange :—	,, A.S.-D.	/ ,, Scarlet T.R. base.
	,, A.S.	/ ,, Orange G.R. base.
For scarlet :—	,, A.S.	/ ,, Scarlet G. base.
	,, A.S.	/ ,, ,, R.C. base.
	,, A.S.-D.	/ ,, ,, G. base.
For red :—	,, A.S. }	/ ,, ,, G. base.
	,, A.S.-B.S }	/ ,, ,, G. base.
	,, A.S.-D.	/ ,, ,, R.C. base.
	,, A.S.-D.	/ ,, ,, T.R. base.

The Indigo-dyed goods are padded with the usual solutions of the above naphthols and, after quick drying in the hot flue, are printed with chlorate discharges containing diazo-solutions of the appropriate bases. Quantities for these solutions may be calculated from the tables given on pp. 544, 545. After printing, the goods are carefully dried and subsequently treated as already described.

Unfortunately the yellows cannot be printed in combination with the oranges, reds, and scarlets, as none of the bases used for these latter gives anything but a sort of yellow on a prepare of Naphthol A.S.-G. (or later naphthols of similar type) which is essential for yellows and cannot be substituted. If, therefore, a yellow is required in combination with red, scarlet, or orange, it must be obtained by other means and, in this connection, the vat yellows come into consideration. Anthra yellow G.C. and Indanthrene golden yellow G.K. are both fairly satisfactory colours to use if printed by the Leucotrope reduction process (to be described later) which works well in combination with chlorate oxidation discharges if care is taken, in printing, to prevent the colours from working into each other. Blues, greys, and greens may also be obtained from various vat dyestuffs by the same Leucotrope process and provide useful and fast supplementary colours to complete the range of discharge effects on Indigo.



Discharges with Naphthol A.S. and Indanthrene colours on dyed Indigo (I.G.).

The attached pattern illustrates the simultaneous application of oxidising and reducing discharges to dyed Indigo grounds, the red and orange being Azoic colour chlorate discharges whilst the grey is a vat colour printed with Rongalite-Leucotrope.

The Indigo-dyed goods are padded in—

PREPARE.

15 grms. Naphthol A.S.-D.
20 c.c. Turkey red oil (oleine).
22·5 ,, caustic soda 60° Tw.
2 grms. Nekal B.X. dry.

To 1 litre with water,

and, after drying in the hot-flue, are printed with the following colours:—

PRINTING COLOURS.

	Red.	Orange.
Chlorate standard C.P.	770 grms.	770 grms.
Tartaric acid (powdered)	40 ,,	40 ,,
Diazo-solution T.R.	170 ,,	..
Diazo-solution R.	..	170 ,,
Sodium acetate	20 ,,	20 ,,
	1000	1000

Grey.

50	grms.	Indanthrene grey 3 B. double paste fine.
450	,,	neutral starch-tragacanth paste.
200	,,	Rongalite C.L. (containing Leucotrope W.).
260	,,	water.
40	,,	anthraquinone 30 per cent. paste.
1000		

Chlorate Standard C.P.

500	grms.	acetic-starch-tragacanth paste.
400	,,	sodium chlorate.
50	,,	red prussiate of potash $K_3Fe(CN)_6$.
50	,,	water.
1000		

Diazo-solution T.R.

60	grms.	Fast red T.R. base.
60	c.c.	hydrochloric acid 33° Tw.
700	,,	water and ice.

Dissolve and add—

24	grms.	sodium nitrite.
60	c.c.	water.

Allow to stand 20 minutes and make up to—

1 litre

Diazo-solution R.

50	grms.	Fast orange R. base.
75	c.c.	water.
27	grms.	sodium nitrite.

Stir into—

700	c.c.	ice water.
107	,,	hydrochloric acid 33° Tw.

Allow to stand 15 minutes or more, filter, and make up to—

1 litre

After printing, the goods are steamed for 5 minutes in the rapid ager, then washed (or lightly chromed) in cold water to re-oxidise the vat colour and to prevent injury to the Azoic colours by undestroyed Rongalite, finally being passed at 180°–190° F. through a bath of caustic soda (15 c.c. NaOH, 62° Tw., per litre) or a 1 per cent. solution of silicate of soda, followed by a thorough wash in warm and cold water successively. The alkaline treatment in silicate of soda, or caustic soda, serves the double purpose of dissolving out the isatin formed by the oxidation discharges and the alkali-soluble indigo-white compound resulting from the reduction of Indigo by the Rongalite C.L., thus removing from the printed parts all decomposition products and leaving the coloured discharges clear, bright, and permanent.

These styles may be produced equally well with the Brenthols and Caledon colours corresponding to the naphthols and vat dyestuffs above mentioned.

Azoic colours discharged on dyed Indigo by the chlorate process yield

bright fast colours, but they call for careful handling in bulk; the made-up printing colours are rather unstable and, in order to avoid unevenness, they must be prepared as required and printed and steamed without undue delay. The style was always more important on the Continent than in England, and even there has lost much of its importance since the introduction of Variamine blue B., which lends itself admirably to the production of similar, and more brilliant, effects on dark blue grounds.

(4) Prussiate Discharge.

This process is founded on the oxidising action of red prussiate of potash ($K_3Fe(CN)_6$) in presence of caustic soda. It is only applicable to light and medium shades of Indigo, as red prussiate cannot be kept in solution at a strength sufficient to discharge dark shades. The cloth is printed with a thickened solution of red prussiate, and, after drying, is passed through a warm bath of caustic soda, then well washed and, if necessary, soaped. In combination with the diazo compounds of para- and meta-nitraniline, nitro-toluidine, α-naphthylamine, chloranisidine, and o-anisidine, very fine, fast, and brilliant discharge effects are obtained on Indigo-dyed cloth previously prepared in β-naphthol. The nature of the process allows of a fine white being obtained, since the caustic soda removes all excess of naphthol (or diazo compound in the colours).

Prussiate White.

200	grms.	red prussiate of potash.
500	,,	water.
60	,,	starch.
240	,,	4 per cent. tragacanth thickening.
1000		

Boil and cool.

Discharge Red P.

15	grms.	paranitraniline.
75	,,	hot water.
24	,,	hydrochloric acid 36° Tw. Dissolve, and add—
75	,,	ice.
82·5	,,	ice water.
And at 0° C.,		
28·5	grms.	nitrite solution 29 per cent.
510	,,	flour-tragacanth paste.
160	,,	red prussiate (finely ground).
30	,,	sodium acetate.
1000		

Other diazo solutions may be applied similarly. Print on Indigo-dyed cloth prepared in a 2½–3 per cent. solution of β-naphthol; dry and discharge the blue by a 10–20 seconds' run through the discharging bath given below.

Discharging Bath.

100 litres caustic soda 20° Tw.
750 grms. soda-ash.

Used at 20–25° C.

For white alone, the temperature of the discharging bath may be raised to 50° C. Wash well (and soap lightly for colours) after discharging. A run

through dilute sulphuric acid in the cold acts favourably on both ground and discharges; this should be given before soaping.

The prussiate discharge finds only a limited application in practice at the present time.

(5) Freiberger's Nitrate Discharge.[1]

The decolorising action of nitric acid on Indigo has long been utilised as a rough-and-ready test for the purity of Indigo-dyed fabrics; but nitric acid, as such, is not applicable in practice on account of its violent corrosive action on the doctors, printing rollers, and fabrics. Although it has been used to a limited extent in block-printing—chiefly for conversion effects on light Indigos—it has never become of any importance as a discharging agent on a large scale, and is certainly inadmissible in current practice. Nevertheless, when produced on the fibre by the decomposition of nitrates it constitutes a valuable means for obtaining both white and fast coloured discharges on Indigo; and if its liberation be conducted under suitable conditions neither hydrocellulose nor oxycellulose is formed—in a word, it does not attack the fibre.

A 12 per cent. solution of nitric acid acts very slowly on Indigo-dyed goods, but the same strength of acid, if diluted with sulphuric acid of 50 per cent. strength, instead of with water, instantly destroys the Indigo. If the concentration of sulphuric acid is increased to 70 per cent., even 6 per cent. of nitric acid is sufficient to destroy Indigo.

These considerations suggested to M. Freiberger the idea of employing nascent nitric acid liberated from nitrates by the action of a stronger acid. His initial experiments in this direction proved that the liberated nitric acid only acted in a concentrated state and at a relatively high temperature. It was necessary to print colours containing at least 14 per cent. of nitrate of soda, and to effect the liberation of nitric acid by a rapid passage (4 seconds) through sulphuric acid at 80° Tw., heated to, at least, 150° F., followed by a rapid wash and neutralisation in weak alkali. The resulting white was excellent, but the cloth was slightly tendered.

Further experiment showed that a small proportion of nitrite in the nitrate discharge rendered the process more effective; and later both nitrate of lead and nitrate of zinc were found to be equally suitable in particular cases.

Coloured effects may be obtained by adding diazotised amines to the white discharge and printing on Indigo previously prepared in β-naphthol. Yellows and greens are produced by chroming the lead nitrate discharges and mixtures of lead nitrate and Prussian blue, and also by means of Direct colours and vat colours.

The latitude of the Freiberger process is well illustrated by the following formulæ and processes published by the inventor.

Discharge White I.

275	grms.	nitrate of soda.
50	,,	nitrite of soda.
675	,,	British gum thickening.
1000		

Print, dry, and pass through—

$\left\{\begin{array}{ll} 400 \text{ grms. sulphuric acid } 168^\circ \text{ Tw.,} \\ 1000 \quad ,, \quad \text{water,} \end{array}\right.$

at 197° F., for 4½ seconds. Wash well by passing at once through a bath of weaker acid followed immediately by a run through a series of water becks.

[1] *Journ. Soc. of Dyers and Colourists*, 1910, p. 253. *Färb. Ztg.*, 1910, p. 239; 1913, Nos. 1 and 2. *Bulletin de la Société Industrielle de Mulhouse*, 1913, p. 225.

Discharge White II.

400	grms.	nitrate of lead.
50	,,	nitrite of soda.
550	,,	starch-tragacanth paste.

Print and treat as above.

This discharge produces neither hydrocellulose nor oxycellulose, and the discharged parts retain their original strength even after treatment in hot alkalies.

The sulphate of lead remaining on the fibre may be converted into Chrome yellow by a subsequent passage through bichromate of soda.

If the Indigo cloth is previously prepared in β-naphthol it is possible, by the same method, to obtain a red and yellow discharge; but not a good white because of the discoloration of the naphthol ground.

Red and Yellow Discharge.

Prepare the cloth in—

16	grms.	β-naphthol.
16	,,	caustic soda 75° Tw.
30	,,	soluble oil.
1000	,,	water.

Dry and print the following red—

10·5	kilogrammes	discharge paste, containing 300 grms. lead nitrate per kilogramme of tragacanth paste.
2·7	,,	diazo solution (below).
0·300	,,	acetate of soda.
0·700	,,	nitrite of soda.
14·200	,,	

Diazo Solution.

80 grms. paranitraniline
(or 100 ,, paranitro-orthoanisidine),

per litre diazotised with nitric acid, instead of with the usual hydrochloric acid.

After printing, pass through—

400	grms.	sulphuric acid 168° Tw.,
620	,,	water,

at 180° F. for 3 seconds; wash well, chrome, wash, pass through caustic soda ¾° Tw., wash again, and dry. The cutting, washing, chroming, etc., are best conducted in continuous manner.

White Discharge on Indigo prepared in β-Naphthol.—As compared with the chromate discharge which always results in the formation of oxycellulose, and with other oxidation discharges which generally yield an imperfect white, the following formula produces an excellent white discharge on β-naphthol-prepared Indigo cloth, and may therefore be utilised for red and white effects on a blue ground.

Naphthol Prepare.

16	grms.	β-naphthol R.
16	,,	caustic soda 75° Tw.
33	,,	soluble oil.

To 1000 c.c. with water.

Pad, dry, and print:—

through dilute sulphuric acid in the cold acts favourably on both ground and discharges; this should be given before soaping.

The prussiate discharge finds only a limited application in practice at the present time.

(5) Freiberger's Nitrate Discharge.[1]

The decolorising action of nitric acid on Indigo has long been utilised as a rough-and-ready test for the purity of Indigo-dyed fabrics; but nitric acid, as such, is not applicable in practice on account of its violent corrosive action on the doctors, printing rollers, and fabrics. Although it has been used to a limited extent in block-printing—chiefly for conversion effects on light Indigos—it has never become of any importance as a discharging agent on a large scale, and is certainly inadmissible in current practice. Nevertheless, when produced on the fibre by the decomposition of nitrates it constitutes a valuable means for obtaining both white and fast coloured discharges on Indigo; and if its liberation be conducted under suitable conditions neither hydrocellulose nor oxycellulose is formed—in a word, it does not attack the fibre.

A 12 per cent. solution of nitric acid acts very slowly on Indigo-dyed goods, but the same strength of acid, if diluted with sulphuric acid of 50 per cent. strength, instead of with water, instantly destroys the Indigo. If the concentration of sulphuric acid is increased to 70 per cent., even 6 per cent. of nitric acid is sufficient to destroy Indigo.

These considerations suggested to M. Freiberger the idea of employing nascent nitric acid liberated from nitrates by the action of a stronger acid. His initial experiments in this direction proved that the liberated nitric acid only acted in a concentrated state and at a relatively high temperature. It was necessary to print colours containing at least 14 per cent. of nitrate of soda, and to effect the liberation of nitric acid by a rapid passage (4 seconds) through sulphuric acid at 80° Tw., heated to, at least, 150° F., followed by a rapid wash and neutralisation in weak alkali. The resulting white was excellent, but the cloth was slightly tendered.

Further experiment showed that a small proportion of nitrite in the nitrate discharge rendered the process more effective; and later both nitrate of lead and nitrate of zinc were found to be equally suitable in particular cases.

Coloured effects may be obtained by adding diazotised amines to the white discharge and printing on Indigo previously prepared in β-naphthol. Yellows and greens are produced by chroming the lead nitrate discharges and mixtures of lead nitrate and Prussian blue, and also by means of Direct colours and vat colours.

The latitude of the Freiberger process is well illustrated by the following formulæ and processes published by the inventor.

Discharge White I.

275	grms.	nitrate of soda.
50	,,	nitrite of soda.
675	,,	British gum thickening.
1000		

Print, dry, and pass through—

$\begin{cases} \text{400 grms. sulphuric acid 168° Tw.,} \\ \text{1000 ,, water,} \end{cases}$

at 197° F., for 4½ seconds. Wash well by passing at once through a bath of weaker acid followed immediately by a run through a series of water becks.

[1] *Journ. Soc. of Dyers and Colourists*, 1910, p. 253. *Färb. Ztg.*, 1910, p. 239; 1913, Nos. 1 and 2. *Bulletin de la Société Industrielle de Mulhouse*, 1913, p. 225.

Discharge White II.

400	grms.	nitr[illegible]
50	,,	nitr[illegible]
550	,,	starch tragacanth paste.

Print and treat as above.

This discharge produces neither hydrocellulose nor oxycellulose, and the discharged parts retain their original strength even after treatment in hot alkalies.

The sulphate of lead remaining on the fibre may be converted into Chrome yellow by a subsequent passage through bichromate of [illegible].

If the Indigo cloth [illegible] prepared in β-naphthol [illegible] [illegible]sible, by the same method, to [illegible] [illegible]d white because of the discolora[illegible] [illegible] [illegible] grou[illegible]

Red and Yellow Discharge.

Prepare the cloth in—

16	grms.	β-naphthol.
16	,,	caustic soda 75° Tw.
30	,,	soluble oil.
1000	,,	water.

Dry and print the following red—

10·5	kilogrammes	discharge paste, containing 300 grms. lead nitrate per kilogramme of tragacanth paste.
2·7	,,	diazo solution (below).
0·300	,,	acetate of soda.
0·700	,,	nitrite of soda.
14·200	,,	

Diazo Solution.

80 grms. paranitraniline
(or 100 ,, paranitro-orthoanisidine),

per litre diazotised with nitric acid, instead of with the usual hydrochloric acid.

After printing, pass through—

400	grms.	sulphuric acid 168° Tw.,
620	,,	water,

at 180° F. for 3 seconds; wash well, chrome, wash, pass through caustic soda $\frac{3}{4}$° Tw., wash again, and dry. The cutting, washing, chroming, etc., are best conducted in continuous manner.

White Discharge on Indigo prepared in β-Naphthol.—As compared with the chromate discharge which always results in the formation of oxycellulose, and with other oxidation discharges which generally yield an imperfect white, the following formula produces an excellent white discharge on β-naphthol-prepared Indigo cloth, and may therefore be utilised for red and white effects on a blue ground.

Naphthol Prepare.

16	grms.	β-naphthol R.
16	,,	caustic soda 75° Tw.
[illegible]		soluble oil.

WHITE Z.B.

5,000	grms.	zinc nitrate 168° Tw.,
13,000	,,	starch-tragacanth paste,
1,000	,,	boric acid,
19,000		

and the preceding paranitro-orthoanisidine red ; dry, steam 4 minutes, and pass through an acid bath containing 36 per cent. sulphuric acid at 175° F. for 3 seconds ; wash immediately and neutralise in dilute silicate of soda.

In the absence of boric acid, which exercises a remarkable action in decomposing the naphtholate of soda, only an imperfect white discharge is obtained similar to that resulting from other oxidation discharges.

Still better results are obtained by a process the reactions of which are analogous to those which take place in the lead chambers during the manufacture of sulphuric acid. A solution of the oxides of nitrogen in concentrated sulphuric acid acts very energetically on Indigo in presence of sulphur dioxide ; and by mixing sulphites or hydrosulphites with the nitrate-nitrite discharge a much better white is ensured on naphtholated Indigo blues.

Any sufficiently soluble nitrate may be employed as the base of the discharge. It has been found that the addition of certain weak acids, or their salts, promotes the rapid decomposition of the nitrates during the cutting operation in sulphuric acid. In this connection it is advantageous to add small quantities of acetate of alumina and formic acid along with the boric acid and sulphites already mentioned. Stronger acids give brownish whites owing to the premature formation of nitric acid. Moreover, all excess of naphthol beyond the quantity strictly necessary for combining with the diazo compounds must be carefully avoided. For paranitro-orthoanisidine (the best red for the purpose) it is sufficient to prepare the goods in a solution containing as little as 10 grms. β-naphthol per litre, and it is advisable also to replace almost entirely the caustic soda by castor oil soap (soluble oil). By these means the unsightly white aureoles that frequently surround the red discharges are avoided. Their occurrence may be further guarded against by using acetate of lead in place of acetate of soda to neutralise the free acid in the diazo solutions. Borate of zinc may also be employed instead of free boric acid ; the object throughout being to avoid the presence of undue quantities of very soluble elements in the printing paste—elements which run during steaming, and are the direct cause of aureoles.

In practice the above principles are applied in the following recipes by means of which Freiberger has successfully printed large quantities of Indigo discharges :—

NAPHTHOL PREPARE.

10	grms.	β-naphthol.
8	,,	caustic soda 75° Tw.
33	,,	soluble oil.

To 1000 c.c. with water.

Pad the Indigo cloth, dry, and print:—

DISCHARGE WHITE.

400	grms.	pure zinc nitrate.
53	,,	boric acid.
547	,,	starch paste 15 per cent.
10	,,	potassium sulphite 90° Tw.
25	,,	acetate of aluminium 14° Tw.

And immediately before printing—
12 grms. formic acid 85 per cent.

1047

RED DISCHARGE.

180 grms. lead nitrate standard {317 grms. lead nitrate. / 683 ,, starch paste.}
500 ,, tragacanth thickening.
500 ,, thick starch-tragacanth paste.
270 ,, diazo solution.
80 ,, borate of zinc paste.
78 ,, sodium nitrite.

1608

BORATE OF ZINC.

{1350 grms. zinc sulphate.
2990 ,, borax.}
Dissolve separately, precipitate, and filter to 7380 grms.

DIAZO SOLUTION.

{84·5 grms. paranitro-orthoanisidine.
150 ,, water.
167 ,, nitric acid 66° Tw.}
250 ,, ice and water.
{37·8 ,, sodium nitrite.
156·3 ,, water.}

845

After printing and drying, the goods are cut, or discharged, by passing for $2\frac{3}{4}$ seconds through sulphuric acid 72° Tw. at 175° F., followed by the customary washing, etc.

In the case of a discharge orange with nitrotoluidine the goods are aged for 5 minutes before cutting in acid.

For a yellow discharge in combination with red and white the following recipe may be used:—

YELLOW DISCHARGE.

{317 grms. lead nitrate.
650 ,, tragacanth paste.}
Dissolve, cool, and add—
33 grms. potassium sulphite 90° Tw.

1000

After cutting in acid as above, rinse, pass for 20 seconds through silicate of soda $1\frac{1}{2}$° Tw. at 190° F., wash and develop the chrome yellow in a bath of acidulated bichromate of soda.

Discharge Reserves on Indigo.—An interesting modification of the Freiberger process consists in mixing powerful reducing agents, such as sulphites, hydrosulphites, and stannous oxide, with the nitrate discharges, in fairly large proportion. In this way a colour is obtained which not only discharges an Indigo ground, but is capable also of resisting an over-print or cover of Azoic colours (paranitraniline, etc.).

By adding free alkali to a colour thus composed, together with vat dyestuffs and certain Direct dyestuffs, it is possible to produce a variety of coloured discharge effects on a figured ground of blue and red. Thus—

WHITE DISCHARGE-RESERVE.

300	grms.	nitrate of lead standard (see Red discharge, p. 601).
65	,,	hydrosulphite-formaldehyde.
65	,,	starch-tragacanth paste.
430		

INDANTHRENE YELLOW DISCHARGE-RESERVE.

60	grms.	Indanthrene Yellow R. extra concentrated.
120	,,	stannous oxide paste.
50	,,	glycerine.
670	,,	alkaline thickening.
180	,,	nitrate of soda.
{30	,,	nitrite of soda.
{30	,,	water.
1140		

ALKALINE THICKENING.

7·5	kilogrammes	dextrine.
12·3	,,	gum arabic 1 : 1.
5	litres	water.
40	,,	caustic soda 90° Tw.

Heat to 160° F.

DIRECT YELLOW DISCHARGE-RESERVE.

150	grms.	Diamine gold.
300	,,	boiling water.
1550	,,	nitrate of lead standard (see Red discharge, p. 601).
100	,,	glycerine.
2100		

A green is obtained by mixing Prussian blue with the direct yellow ; and equally a blue discharge resist, by replacing Indanthrene yellow by Indanthrene blue.

The discharge-reserves are printed and dried ; then over-printed with an Azoic red discharge, steamed and cut, etc., as described. The red discharges the Indigo ground, and is itself discharged wherever it falls over the discharge-resists, which cut away both blue ground and red cover print, thus producing clear-cut coloured objects on a red and blue patterned ground.

The Freiberger process is cheaper than any other ; and, as the colours are specially adapted for discharging very dark blues and keep well, it is frequently preferred for continuous working on the large scale. It lends itself to a greater variety of effects than other processes, and, once the initial difficulties connected with the use of strong acid are overcome, it is freer than the older methods from the defect of tendering the fibre.

Reduction Discharges on Indigo.

According to Aubert, Frossard, and Fleischer (*Revue générale des matières colorantes*, 1907, pp. 419, 422), perfect whites can be obtained on Indigo and Thio-indigo by means of the hydrosulphite-formaldehydes. These compounds

are thickened and printed on the dyed material, which, after drying, is steamed for 3–5 minutes at 102° C. in air-free steam, then passed at once through a hot bath of caustic soda, and finally soured, washed, and soaped. Another method is to pass the steamed goods through a hot bath of bisulphite of soda before the treatment in alkali. Soda-ash may also be used.

Aubert recommends the following proportions for the white discharges:—

WHITE DISCHARGE I.

600	grms.	hydrosulphite-formaldehyde.
400	,,	50 per cent. gum Senegal.
1000		

Print, dry, steam as described; pass one minute through a bath at 75° C. containing 10 per cent. bisulphite of soda, and then directly afterwards, for 50–60 seconds, through a bath at 75° C. containing 10 per cent. caustic soda. Finally sour, wash, and soap.

WHITE DISCHARGE II.

200	grms.	hydrosulphite-formaldehyde.
200	,,	gum Senegal 50 per cent.
420	,,	50 per cent. China clay paste.
180	,,	saturated solution of bisulphite-acetone.
1000		

Print, dry, steam in the hydrosulphite ager for 3–4 minutes, and then run through a boiling bath containing 10 grms. soda-ash per litre. Wash, sour, wash, and soap lightly. The bisulphite-acetone may be replaced by a mixture of 10 grms. ferrous sulphate or ferric chloride and 10 grms. nitrite of soda, but the resulting white is not so pure.

It is imperative, with these discharges, to wash the goods in alkali immediately after steaming, as otherwise the Indigo begins to re-oxidise. The rapidity with which this re-oxidation takes place renders the process a delicate one, and one difficult to control on the large scale, and it was, at first, the main obstacle to the general adoption of the hydrosulphite discharges on Indigo. It is evident that to secure regular results from hydrosulphite alone special arrangements are necessary in order to ensure that the printed cloth has an uninterrupted run through the whole process. If, after steaming, the printed goods are allowed to lie before washing-off in alkali, the purity of the whites is either impaired or destroyed altogether according to the length of time the goods are exposed to the air; hence any breakdown in the continuity of the process results in considerable loss. Fortunately these drawbacks were soon overcome, and the hydrosulphite process is now in general use.

The first improvement consisted in the addition of anthraquinone to the discharge pastes—an addition which, along with zinc oxide and neutral acetin, made it possible to allow the goods to lie for about half an hour between the steaming and washing-off operations. The presence of anthraquinone improves the whites and renders them more stable in the air by retarding the re-oxidation of the indigo-white, its action being due probably to the formation of oxyanthranol, which, by becoming oxidised first, protects the indigo-white for a certain time.

If the printed goods cannot be washed off immediately after steaming, it is advisable to wrap them up and store them in a warm dry place. Whenever possible, however, the washing-off in alkali should be proceeded with at once.

The following recipe will serve to illustrate the composition of a modified discharge white :—

DISCHARGE WHITE H.A.

{200	grms.	hydrosulphite-formaldehyde.
{580	,,	British gum thickening.
Heat to dissolve, cool, and add—		
{75	grms.	zinc oxide.
{75	,,	water.
50	,,	anthraquinone paste 30 per cent.
20	,,	acetin (neutralised with soda).
1000		

Print on dark Indigo blue, dry, steam 4 minutes at 102°–104° C. in air-free and fairly dry steam, run at full width through a boiling 1 per cent. solution of silicate of soda, and finally wash and dry.

Notwithstanding the great improvement effected by the use of anthraquinone, the hydrosulphite process still left much to be desired, and it was not until the introduction of the Leucotropes that it was finally put on a thoroughly practical basis.

The Leucotrope Process.—The Leucotrope process of discharging Indigo differs from the earlier hydrosulphite processes in that the indigo-white produced on the fibre is at once converted into stable yellow compounds, which are soluble or insoluble in alkalies according to circumstances. The means whereby these results are brought about were patented by the Badische Anilin und Soda Fabrik, who, in January 1910, put on the market the two products most suitable for the purpose, namely Leucotrope W. and Leucotrope O. These two products belong to a class of bodies which consist of compounds of certain tertiary bases with benzyl chloride, and its substitution products.

The principle of the Leucotrope process is, briefly, as follows :—When compounds of benzyl chloride with dimethylaniline, methylethylaniline, methylphenylaniline, dimethylmetamidophenol, etc., are brought into contact, in presence of zinc oxide, with indigo-white, first produced on the fibre by the hydrosulphite discharge, they form brilliant reddish-yellow dyestuffs, which, being fast to acids, alkalies, air, and soap, are suitable for the production of yellow discharge effects on Indigo-dyed cloth. Leucotrope O. (dimethylphenylbenzylammonium chloride) is a member of this series.[1]

On the other hand, if the benzyl radicle in the above compounds is replaced by benzyl with a sulphonic group or groups substituted in the nucleus, a second series of Leucotropes is obtained ; and these bodies—of which Leucotrope W. (the calcium salt of disulphonated Leucotrope O.) is one—also combine with indigo-white to form yellow dyestuffs which, while unaffected by air and moisture, are very soluble in alkalies, and are therefore well suited to the production of white discharges on Indigo.

The stability, in moist or dry air, of both the soluble and insoluble yellow derivatives of indigo-white dispenses with the necessity for washing the printed goods in alkali immediately after steaming, a great practical advantage over the older hydrosulphite discharges.

As compared with the oxidation discharges (chromate and chlorate), the Leucotrope-hydrosulphite discharge possesses a still greater advantage, viz. that the deepest shades of Indigo can be discharged to a pure white, in either the heaviest or lightest of patterns, without any fear of tendering the cloth in the slightest degree.

[1] K. Reinking, *Jour. of Soc. of Dyers and Colourists*, Dec. 1910.

Rongalite C.L., Hydrosulphite C.L., and Hyraldite C.L. are mixtures of Leucotrope W. with Rongalite C., Hydrosulphite N.F. conc., and Hyraldite A. respectively. They may be applied in exactly the same way as for ordinary hydrosulphite discharges.

In applying the Leucotropes, the Indigo-dyed cloth is printed with any of the following discharge pastes, all of which are suitable for ordinary dark shades of blue.

Strong Discharge White (for fine patterns).

160	grms.	zinc oxide paste 50 per cent.
100	,,	Leucotrope W.
240	,,	hydrosulphite-formaldehyde.
40	,,	anthraquinone paste 30 per cent.
460	,,	British gum thickening.
1000		

For heavier patterns and lighter shades of Indigo, the above may be reduced with thickening as required.

White Discharge with Rongalite C.L.

160	grms.	zinc oxide paste 50 per cent.
40	,,	anthraquinone paste 30 per cent.
200	,,	Rongalite C.L.
600	,,	British gum thickening.
1000		

Yellow Discharge.

460	grms.	British gum thickening.
200	,,	hydrosulphite-formaldehyde.

Dissolve, cool, and add—

100	grms.	Leucotrope O.
40	,,	anthraquinone paste 30 per cent.
200	,,	zinc oxide paste 50 per cent.
1000		

Blue Discharge.

{100	grms.	Indanthrene blue G.C.D. paste.
{200	,,	alkaline thickening (for Indigo).

Mix, and add—

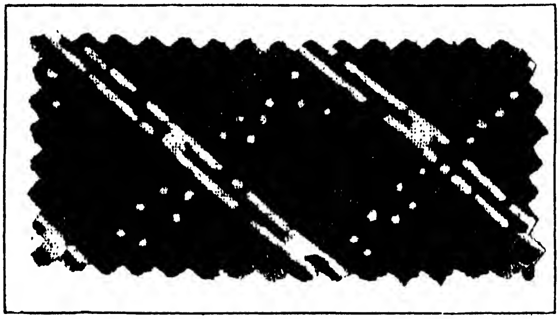
200	grms.	hydrosulphite-formaldehyde.
500	,,	alkaline thickening (for Indigo).
1000		

All the above printing pastes are very stable; they will keep in good condition for a fortnight at least.

After printing, the goods are dried, and then steamed for 4–5 minutes in the rapid ager at 102°–104° C. They are then run, at full width, through a boiling 1–2 per cent. solution of silicate of soda, well washed, and finally dried.

If a blue discharge is printed together with white and yellow discharges, it is advisable to treat the goods in alkali immediately after steaming, since the blue contains no Leucotrope.

In place of silicate of soda, corresponding quantities of soda-ash, caustic soda, or milk of lime may be employed in the stripping bath.



White: Rongalite C. + Leucotrope W.
Yellow: „ „ „ O.
(I.G.).

The pattern shown here was produced by the method and formulæ given below:

WHITE DISCHARGE.

600	grms.	glue-barytes thickening.
150	„	zinc oxide 50 per cent. paste with water.
200	„	Rongalite C.L.
40	„	anthraquinone 30 per cent. paste.
10	„	water.
1000		

YELLOW DISCHARGE.

80	grms.	zinc oxide.
30	„	glycerine.
100	„	water.
500	„	British gum 1 : 1
100	„	Rongalite C.
100	„	water.
40	„	anthraquinone 30 per cent. paste.
50	„	Leucotrope O.
1000		

GLUE-BARYTES THICKENING.

65	grms.	glue.
165	„	water.

Soak until soft, then add—

40	grms.	wheat starch.
60	„	water.

Boil and mix in well—

670	grms.	blanc fixe 50 per cent. paste ($BaSO_4$).
1000		

Print on Indigo-dyed goods, steam, and treat in silicate of soda or, when vat colour discharges are present, in caustic soda, as already described.

The feature of this white discharge is that during the steaming operation formaldehyde splits-off from the Rongalite and by coagulating the glue fixes the barium sulphate or blanc fixe on the fibre as a pigment, thus enhancing the brilliancy of the white.

Red and reddish-orange discharges in multicolour combinations with white and yellow may be obtained by printing chlorate discharges containing suitable diazo-compounds along with the foregoing Leucotrope O. and W. discharges on Indigo-dyed cloth prepared in Naphthol A.S. or Brenthol A.S. or their homologues.

Certain of the anthraquinone dyestuffs also lend themselves to the production of fast-coloured discharges on Indigo-dyed grounds by the Leucotrope process. The printing colours contain *no alkali*, being prepared from neutral thickening, Rongalite C.L. (which contains Leucotrope W.) and anthraquinone only, together with, of course, the dyestuff in paste or pigmentary form. Made-up in this way they resist the action of Leucotrope in steaming. The necessary alkali for their complete reduction and fixation is provided, after steaming, by a final passage through the usual hot caustic soda bath. Such colours are suitable for printing simultaneously with Leucotrope discharges on plain dyed Indigo grounds, or with both Leucotrope and chlorate Azoic colour discharges on naphtholated Indigo goods.

ANTHRAQUINONE VAT DYESTUFF DISCHARGES ON INDIGO.

	GREY.	BLUE.	GREEN.
Indanthrene grey 3 B. double paste . .	50 grms.	..	..
Indanthrene blue G.C.D. double paste .	..	150 grms.	..
Indanthrene brilliant green B. double paste	..	..	150 grms.
Neutral starch–British gum paste . .	450 ,,	300 ,,	300 ,,
Rongalite C.L.	200 ,,	200 ,,	200 ,,
Water	260 ,,	310 ,,	310 ,,
Anthraquinone 30 per cent. paste . .	40 ,,	40 ,,	40 ,,
	1000 grms.	1000 grms.	1000 grms.

Print, steam for 3–4 minutes at 102° C., pass through a bath of caustic soda (15 c.c. NaOH, 62° Tw., per litre) at 85° C., wash, and dry.

One or two Indanthrene yellows may be used also by the foregoing process, but they are liable to irregularities and are rarely so employed. Any suitable Caledon or Cibanone dyestuff, too, may replace the above Indanthrenes without loss of effect; in fact, wherever Indanthrene colours are mentioned in the following pages, it may be taken that the corresponding products of the Caledon group are equally applicable.

Although fine effects are obtainable from combined styles embodying both Azoic and vat colour discharges, these styles are not in general use; they require very careful handling and a good deal of supervision and, consequently, remain the monopoly of a few firms. Indeed, except in a very few works, the Leucotrope process itself is restricted to the production of white effects on Indigo. The yellow given by Leucotrope O., whilst fast to washing, is extremely loose to light, a disadvantage which renders it unfit for the highest class of work.

The Haller Process.—This process for vat colour discharges on Indigo, combines the Rongalite C.L. or Leucotrope method of discharging dyed Indigo

with the original method of fixing anthraquinone vat dyestuffs by means of ferrous sulphate and stannous chloride. It is applicable to a wide range of Indanthrene, Caledon, and Cibanone colours and yields results superior alike in depth, variety, and regularity to those obtained by any other reduction process of discharging Indigo. The lack of a suitable anthraquinone red is supplied, as in other cases, by an Azoic red chlorate discharge printed on Indigo-dyed cloth prepared with Naphthol A.S., etc., and, if desired, bright oranges may be obtained by similar means. The printing colours and naphthol prepares are exactly the same as those described under the "Chlorate Discharge."

The process as published by Haller (*Handbuch des Zeugdrucks*, Georgievics, Haller, and Lichtenstein, p. 600, 1930) is as follows:—

WHITE DISCHARGE.

13,000	grms.	British gum (dry).
10,000	,,	water.
3,500	,,	grape sugar (glucose).
5,000	,,	Rongalite C.L.
3,600	,,	zinc oxide.
3,000	,,	water.
500	,,	rape-seed oil.
500	,,	turpentine.
1,800	,,	gum 1 : 1.
40,900		

STANDARD FOR COLOUR DISCHARGES (Standard C.D.).

7,100	grms.	white discharge, above.
500	,,	ferrous sulphate.
200	,,	stannous chloride.
200	,,	glycerine.
8,000		

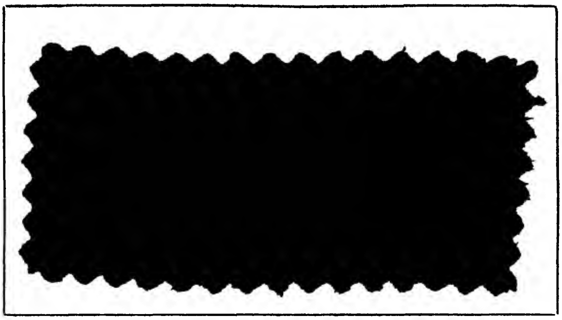
PRINTING COLOURS (Example).

600	grms.	Indanthrene blue G.C.D. double paste.
600	,,	Indanthrene blue R.S. double paste.
8,700	,,	standard colour discharge, above.
500	,,	Rongalite C.L.
10,400		

Print on Indigo-dyed goods, steam for 4–5 minutes in the rapid ager, pass for ½ minute through caustic soda, 33° Tw., at 180° F., wash, sour, wash, and soap.

The majority of Indanthrene, Caledon, and Cibanone dyestuffs may be utilised by this process for the production of extremely fast-coloured discharge effects on dark Indigo grounds. White discharges of excellent quality are obtained by means of the Leucotrope discharges already described, and, in the case of various vat yellows, satisfactory results may be obtained without the aid of ferrous sulphate or stannous chloride which, however, are to be recommended.

A simpler method of applying the Haller process is exemplified by the pattern illustrated opposite, the colour for which is made up directly, and without glucose.



Indanthrene Blue R.S. discharged on dyed Indigo (I.G.).

PRINTING COLOUR.

100	grms.	Indanthrene blue R.S. double paste fine.
225	,,	British gum thickening 1 : 1.
100	,,	zinc oxide 50 per cent. paste.
20	,,	anthraquinone 30 per cent. paste.
40	,,	Rongalite C.
100	,,	Rongalite C.L.
250	,,	water.
150	,,	ferrous sulphate.
15	,,	stannous chloride.
1000		

Print, steam, etc., as already described.

The Haller process yields superior results, giving clean-cut discharges in full shades which stand out clearly from the background. Combinations of Indanthrene colours and Azoic colours (chlorate discharge) are printed on naphtholated Indigo goods, no other alteration in process being necessary.

Discharging of Indigo with Glucose.—An interesting modification of the Leucotrope discharge process, based upon the reducing action of glucose and caustic soda, was suggested by A. Scheunert and U. Vosnessenski.[1] The idea was not new, but its application was novel, and it was extended to provide for the production of coloured discharges. In its simplest form the process consists in printing a discharge containing 300 grms. of glucose and 700 grms. of thickening, followed by a passage through boiling caustic soda 52° Tw., and then immediately by a wash in boiling water. The addition of zinc oxide and Leucotrope W. improves the results; and a short steaming before the alkaline treatment is also advantageous.

To obtain coloured effects it is only necessary to add colouring matters that resist the action of boiling caustic soda, and remain unimpaired by the reduction that destroys the Indigo. Of these the most important are the vat colours of the Indanthrene type, and the Insoluble Azoic colours produced on the fibre. Under ordinary conditions Leucotrope does not react with diazo salts, and its presence in the colour ensures a perfect discharge of the Indigo, and does not apparently affect the coupling of the diazo with β-naphthol. When fully developed the Insoluble Azoic colours are, as is well known, particularly difficult to reduce except by the most powerful reducing agents, such as the hydrosulphites. In the present process the colours are developed before

[1] *Bulletin de la Soc. Industrielle de Mulhouse*, p. 263, May 1920.

reduction takes place, and experience has shown that they withstand perfectly the reducing action that arises during the passage through caustic soda. On the large scale the glucose-alkali discharge has been worked with success at the Three Mountains Works (Prochoroff), near Moscow. The particulars given below illustrate the methods in use.

White Discharges.

	I.	II.
Glucose	300 grms.	300 grms.
Zinc oxide	..	100 ,,
Leucotrope W.	..	50 ,,
Thickening (British gum)	700 ,,	550 ,,
	1000	1000

Azoic Colour Discharges.

	I.	II.
Diazo solution	150 grms.	250 grms.
Glucose	200 ,,	200 ,,
Leucotrope W.	50 ,,	50 ,,
Thickening	600 ,,	500 ,,
	1000	1000

Recipe I. is used for a-naphthylamine, chloranisidine, and benzidine discharges.

Recipe II. is used for Azo rose B.B. (20 grms. per litre) or p-nitro-o-anisidine discharges.

Vat Colour Discharges.

250	grms.	Indanthrene colour in paste.
300	,,	glucose.
450	,,	thickening.
1000		

The above colours are printed on Indigo-dyed cloth (prepared in β-naphthol for the Azoic colours), dried, and passed first through a bath of boiling caustic soda 52° Tw., and then directly into boiling water, the two processes being continuous. The treatment is regulated to occupy 1–1½ minutes.

It was found subsequently in the case of the vat colours that much brighter and deeper colours could be obtained, together with a reduction in the strength of the caustic soda bath, by replacing a portion of the glucose with stannous chloride. Thus:—

250	grms.	colouring matter in paste.
100	,,	glucose.
50	,,	stannous chloride.
600	,,	thickening.
1000		

Print, dry, and discharge in caustic soda 32°–42° Tw. at the boil.

The advantages of the glucose discharge process consist in its comparative cheapness, in the stability of the colours, and in the certainty of obtaining a good white alongside an Azoic red—this last an important point.

Titanium Discharges on Indigo.—The application of the powerful reducing

action of titanous salts to the discharging of Indigo was patented by E. Knecht and Peter Spence & Sons, Ltd.

On medium shades of Indigo good results have been obtained in printing by this method, but hitherto practical difficulties have prevented its employment for dark shades.

All the titanous salts reduce Indigo rapidly, even on drying, but, with the exception of the sulphocyanide, they all either tender the cloth, or are too unstable for use as printing pastes.

The sulphocyanide is made directly by the double decomposition of titanous sulphate and barium sulphocyanide ; and as the precipitated barium sulphate is in an extremely fine state of division, and has no action on the reducing powers of the titanous salt, it is allowed to remain, the whole mixture being simply thickened with British gum and printed.

Discharge White T.

1000	grms.	titanous sulphate solution [15 per cent. $Ti_2(SO_4)_3$].
500	,,	barium sulphocyanide.
150	,,	British gum.
1650		

Boil till smooth.

Print on a medium shade of Indigo, dry, and strip off the reduced Indigo by passing at once through a boiling solution of caustic soda 2° Tw. Wash well and dry.

A short steaming may be given before stripping if desired, but it affects the ultimate result very slightly, and is, moreover, apt to tender the cloth. The addition of glucose is an advantage in this latter connection.

The fact that titanic hydrate is deposited on the discharged parts of the cloth renders possible the production of white and coloured discharge effects. For this purpose a Leucotrope white is printed alongside white discharge T., the goods are steamed and stripped in the usual way, and then washed well and dyed up in mordant colours such as Alizarin, Alizarin orange, Persian berries, Quercitron bark, etc. The titanic hydrate acts as a mordant for these dyestuffs, yielding red, orange, yellow, and gold respectively, whereas the parts upon which the Leucotrope discharge is printed remain white.

Conversion Effects on Indigo.—A conversion effect depending on the discharging of both dyed and printed Indigo is obtained in the following way. A green composed of Indanthrene yellow G. and Indigo in combination with caustic soda and hydrosulphite-formaldehyde is printed on a light Indigo-dyed ground. The goods are steamed for 3 minutes at 102° C., and then well washed in cold water to develop the mixed green. This gives a green pattern on a light blue ground. If a Chromate white discharge is now printed over the green and blue, it discharges the blue completely and converts the green into a yellow by destroying its blue element. If the pattern printed in green be a check and the pattern in white a large spot, the effect produced is that of a yellow and white check spot on a blue and green check ground, the check being continuous all over. A similar effect is produced by printing Indanthrene yellow alone, but in that case the green is too weak to contrast well with the blue ground.

Other vat colours may be used in the same way to give a variety of similar effects. In fact, the various modifications of the different Indigo discharge processes are so numerous that it is impossible to enumerate more than one or two in a work of this size.

Discharging of Vat Dyestuffs other than Indigo.

Most members of the Indigoid group of vat dyes—the Ciba, Durindone, and Algole series—are readily dischargeable by means of hydrosulphites and Leucotrope W. in a manner analogous to that employed for discharging Indigo. In many cases the Indigo discharges already described are equally suitable for these colours. The dyeing of the cloth may be performed either in vats, jiggers, etc., according to the ordinary methods in current use; or by slop-padding in a mangle through reduced solutions of the dyestuffs made up in one or other of the following ways:—

PADDING BATHS.

	I.	II.
Dyestuff in paste	15–30 grms.	15–30 grms.
Warm water	400 ,,	400 ,,
Caustic soda 76° Tw.	15 ,,	15 ,,
Oleine 40 per cent.	5 ,,	5 ,,
Mix and strain through a fine cloth and add—		
Anthraquinone paste 10 per cent.	10 ,,	10 ,,
Hydrosulphite conc. powder	7–10 ,,	10 ,,
Formosul or Britulite	.. ,,	5 ,,
Tragacanth thickening	50 ,,	50 ,,
Make up to	1000 c.c.	1000 c.c.

Recipe II. is slightly more expensive than I., but it yields rather darker shades which are also faster to soaping.

The goods are padded at 70°–85° F., dried in the hot flue, and then steamed at 214°–216° F. for 4 minutes, followed by a thorough wash in cold water, or by a light chroming. A final soaping at the boil is necessary to the full development of the shades.

The presence of anthraquinone improves the stability of the leuco compound, and that of oleine assists considerably in its solution; the two bodies together facilitate the production of even and regular shades. The addition of tragacanth thickening operates in the same direction. The process is not easy to carry out successfully without the exercise of careful supervision, and good results can only be obtained by observing the following directions: —(1) the cloth must pass through the colour solution as rapidly as is consistent with its thorough penetration—an immersion of 3–5 seconds is ample, the goods being padded at a speed of 25–30 yards per minute; (2) the feed liquor must be distributed evenly across the full width of the colour box by means of a perforated iron pipe, and it must run in continuously, being so regulated as to maintain the liquor at a constant level; (3) rubber bowls are advisable to minimise risks of frothing, and froth is best prevented from getting on the cloth by arranging for the latter to enter the liquid between two boards, placed as close together as possible, and dipping beneath the surface of the liquor. The degree of alkalinity exercises a great effect upon the depth and evenness of the shades, and it ought not to exceed the quantity required for the solution of the leuco compound. Too much caustic soda diminishes the affinity of the dyestuff for the fibre, and the resulting shades are reduced in depth in proportion to the excess of soda.

Medium shades only are obtainable by padding; darker shades must be dyed on the jigger.

The padded or dyed goods may be printed with any Leucotrope discharge suitable for Indigo (*q.v.*) or with those given below :—

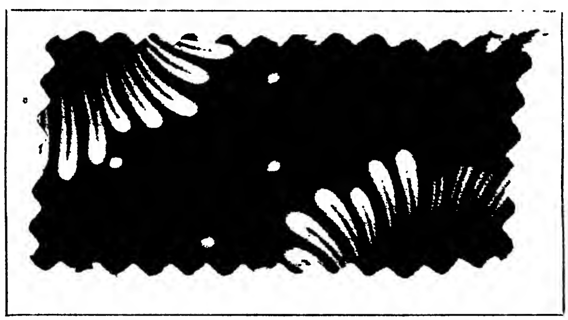
	I.	II.	III.
Zinc oxide 50 per cent. paste .	100 grms.	100 grms.	200 grms.
Blanc fixe 50 per cent. ,, . .	200 ,,	150 ,,	..
Anthraquinone 30 per cent. paste	35 ,,	40 ,,	50 ,,
Britulite or Formosul . . .	50 ,,	75 ,,	200 ,,
Leucotrope W.	25 ,,	75 ,,	100 ,,
Caustic soda 76° Tw.	..	..	50 ,,
British gum thickening and water	590 ,,	510 ,,	400 ,,
Glycerine	..	50 ,,	..
	1000	1000	1000

Discharges I. and II. are for medium shades ; Discharge III. is for dark dyed shades.

After printing, the goods are steamed for 4–5 minutes, in the hydrosulphite ager, then passed through a boiling solution of silicate of soda $\frac{3}{4}$° Tw., and finally soaped at 180° F. Medium and light shades may in many cases be cleared equally well in boiling soap (if it be slightly alkaline) without previous treatment in silicate of soda, and, conversely, soaping may be omitted if silicate is used.

Aniline black may be associated with the white discharges if the precaution be taken to interpose a plain roller working in starch paste (or acidulated starch paste) between the black and white rollers.

Discharge effects of considerable brightness and great fastness may be produced with colours of the Indanthrene, Caledon, and Cibanone groups by applying the Haller process of discharging Indigo (*q.v.*) to dyed grounds of all Ciba, Durindone, and Algole dyestuffs that are capable of being discharged by sulphoxylates and of withstanding a passage through hot strong caustic soda.



White and Cibanone Orange discharges on Ciba Blue 2 B. ground (S.C.I.B.).

The simpler Leucotrope process may also be utilised to the same end, although it is not adapted to so wide a range of Anthraquinone dyestuffs for colour discharges. The pattern shown here consists of a dyed ground of Ciba blue 2 B. printed with a Leucotrope discharge white and an orange discharge made from Cibanone golden orange G.P.

WHITE DISCHARGE.

Any sulphoxylate-leucotrope discharge.

ORANGE.

150	grms.	Cibanone orange G.P.
600	,,	discharge paste X.
80	,,	Discharge salt Ciba W. (Leucotrope W.).
20	,,	Anthraquinone paste 30 per cent.
150	,,	water.
1000		

Discharge Paste X.

{50	grms.	zinc oxide.
{50	„	glycerine.
30	„	Dissolving Salt B. (*q.v.*).
200	„	British gum solution 1 : 1.
120	„	potassium carbonate.
150	„	Hydrosulphite R. conc. Ciba 2 : 1. (or Rongalite C.).
600		

Print, steam for 4–5 minutes in the rapid ager, pass through a bath of caustic soda, 6° Tw., at 160°–175° F., and finally wash, soap at the boil, wash, and dry.

A process that has given good results in practice on grounds of selected vat dyestuffs uses the following discharge paste :—

Discharge Paste D.

150	c.c.	water.
30	grms.	Indian corn starch.
30	„	tapioca flour.
50	„	British gum (dry).
25	„	Dissolving Salt B.

Mix and add—

300	c.c.	water.
62·5	grms.	glycerine.
87·5	„	potassium carbonate.
37·5	„	soda-ash.

Boil, cool to 120° F., and add—

100 grms. Formosul or Rongalite C.

Cool completely and make up to—

700 c.c.

The printing colours are prepared by mixing suitable vat dyestuffs with the foregoing discharge paste plus an addition of Leucotrope W. In practice the following colours have been found to resist the action of Leucotrope W. and Formosul under the conditions of the process: Caledon brilliant purple R.R., Indanthrene golden yellow G.K., Helindone orange R., Indanthrene brilliant blues 3 G. and R., Indanthrene grey 3 B., Anthra yellow G.C., Hydron scarlet B.B., Hydron pink F.B., and all mixtures of these colours.

Example of Printing Colour.

{700 c.c. Discharge paste D.
{150 grms. Caledon brilliant purple R.R. double paste.

Mix, warm to 120° F., cool, and add—

80 grms. Leucotrope W.

Make up to 1 litre.

Other colours are made up similarly with 150 grms. of vat colour double paste, or 300 grms. single paste, per litre.

After printing, the goods are steamed *twice* for 3–4 minutes at 212°–214° F. in a rapid ager and then, in a continuous manner, passed successively through a chrome bath (½ oz. $Na_2Cr_2O_7$ per gallon or 3 grms. per litre), a rope washing

machine, and a rope soaping range, in which latter they are soaped at the boil for 10 minutes in an alkaline soap solution.

Grounds of medium and light shades suitable for discharging may be dyed by any of the ordinary methods with—

Indanthrene Yellow F.F.R.K.	Ciba Scarlet G.
,, Brilliant Orange R.K.	,, Yellow G.
,, Brown G.	,, Brown G.
Ciba Blue 2 B.	Helindone Scarlet R.
,, Grey B.	Anthra Scarlet G.G.
,, Orange G.	Thioindone Green G.
,, Violets B., 2 B., 3 B.	

and others of similar type and properties.

Indigosol Discharges on Vat Colour Grounds.

The strictly limited range of fast-colour discharges on vat colour grounds obtainable from the foregoing processes has been very greatly extended of late by the important observation that *all* the Indigosol dyestuffs lend themselves to the production of coloured discharges by the Rongalite-Leucotrope method and that they give a much better colour yield than do ordinary vat colours applied by the same method. The Indigosols withstand the action of Rongalite-Leucotrope to a remarkable degree and, as very few ordinary vat colours possess that property, this means that the possibilities of the process are trebled in respect of discharge colours. The ground shades must still be dyed with the dischargeable vat dyestuffs already enumerated, or obtained by padding with Indigosols which are subsequently developed by the usual methods. All the Indigosols with the exception of Indigosol green I.B.A. and the Indigosol golden yellows I.R.K. and I.G.K. are available for this purpose.

The process, which is due to Durand & Huguenin, S.A., of Bâle, is carried out in the following manner: The discharge colours, consisting of Indigosol dyestuff, Hydrosulphite N.F., and Leucotrope are printed on grounds dyed with dischargeable vat colours or with fully developed Indigosols. After drying, the goods are steamed for 8 minutes in the rapid ager in order to effect the discharge of the ground shades, and then passed through a hot acid oxidising bath for the purpose of completing the development of the printed Indigosol discharges. Hereafter the goods follow the usual routine of vat colour styles, *i.e.* washing, soaping at the boil, etc.

The comprehensive range of colours available for the production of discharge effects by this process is amply demonstrated in the following table of recipes:—

WHITE DISCHARGE.

200	grms.	Rongalite C.L.
200	,,	Leucotrope W.
300	,,	British gum 1 : 1.
30	,,	zinc oxide.
50	,,	precipitated chalk.
120	,,	water.
100	,,	caustic soda 72° Tw.
1000		

Other white discharges, already given, are also suitable.

INDIGOSOL COLOUR DISCHARGES.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Indigosol Golden Yellow I.G.K.	30	..	..	..	..	..	..	..	..
„ „ „ I.R.K.	..	30	..	..	..	..	..	..	..
„ Yellow H.C.G.	..	..	30	..	..	..	..	..	..
„ Orange H.R.	..	..	..	30	..	..	..	..	..
„ Scarlet H.B.	..	..	..	..	30	..	..	..	..
„ „ I.B.	..	..	..	..	..	40	..	..	..
„ Brilliant Pink I. 3 B.	..	..	..	..	..	..	30	..	..
„ Pink I.R. extra	..	..	..	..	..	..	..	20	..
„ Printing Purple I.R.	..	..	..	..	..	..	..	..	30
Glyecine A.	50	50	50	50	50	50	50	50	50
Fibrit D.	..	..	..	..	50	..	..	50	..
Hot water	70	70	70	70	20	60	70	30	120
Dextrine thickening 1:1	300	300	300	300	300	300	300	300	250
Paste together, warm until dissolved, and add whilst warm:—									
Soda-ash	150	150	150	150	150	150	150	150	150
Hydrosulphite N.F. conc.	150	150	150	150	150	150	150	150	150
Leucotrope W.	150	150	150	150	150	150	150	150	150
Zinc oxide 1:1	100	100	100	100	100	100	100	100	100
	1000								

	10.	11.	12.	13.	14.	15.	16.	17.	18.
Indigosol Printing Violet I.B.B.F.	40	..	..	..	..	..	..	..	..
„ O. 4 B.	..	30	..	..	..	..	..	..	..
„ O. 6 B.	..	..	30	..	..	..	..	..	..
„ Printing Blue I.G.G.	..	..	..	30	..	..	..	..	..
„ „ „ I.B.	..	..	..	..	30	..	..	..	..
„ Green I.B.A. paste	..	..	..	..	..	50	..	..	..
„ „ A.B.	..	..	..	..	..	..	20	..	..
„ Brown I.R.R.D.	..	..	..	..	..	..	..	40	..
„ Printing Black I.B.	..	..	..	..	..	..	..	..	40
Glyecine A.	50	50	50	50	50	50	50	50	50
Fibrit D.	..	..	..	..	..	..	50	50	..
Hot water	60	70	120	120	120	50	80	60	70
Dextrine thickening 1:1	300	300	250	250	250	300	250	250	290
Paste together, warm until dissolved, and add whilst warm:—									
Soda-ash	150	150	150	150	150	150	150	150	150
Hydrosulphite N.F. conc.	150	150	150	150	150	150	150	150	150
Leucotrope W.	150	150	150	150	150	150	150	150	150
Zinc white 1:1	100	100	100	100	100	100	100	100	100
	1000								

Print on vat colour dyeings, steam for 5–8 minutes in the rapid ager at 214°–216° F., pass through a bath of

$$\begin{cases} 20 \text{ grms. bichromate of soda,} \\ 30 \text{ c.c. sulphuric acid } 168° \text{ Tw.,} \\ 1000 \text{ ,, water,} \end{cases}$$

at 160° F. to develop the Indigosol discharges, wash thoroughly (neutralise with soda-ash if necessary) and soap for 10 minutes at the boil, wash again, and dry.

As will be seen, the process presents no complications ; nor does it call for the exercise of special care to prevent the printed discharge colours from being washed-out (at least partially) along with the discharged portions of the ground, during the soaping operation, as is liable to occur in the case of other vat colour discharge processes. Compared with these latter, the Indigosol process affords a means of producing a *complete* and unrestricted range of discharge colours in full rich shades, and of an increased brightness which adds considerably to the attractiveness and commercial possibilities of the style. From a practical point of view the process is less interesting than might be supposed, since a greater variety of similar effects are more conveniently obtained by the reverse method of printing ordinary vat colours on undeveloped Indigosol grounds—a resist process to be described later.

The Indigosol-Rongalite-Leucotrope discharge is not adapted to Indigo grounds. Such grounds may, however, be discharged by a chlorate process, described under " The Discharging of Slop-padded Chrome Shades."

Discharging of Anthraquinone Vat Dyestuffs.

As a class, the Anthraquinone dyestuffs may be regarded as undischargeable by any of the usual methods employed for Indigo or Indigoid colouring matters. There are a few exceptions (see preceding list) but, as a general rule, ordinary Leucotrope or chlorate discharges have little or no effect upon dyeings of Indanthrenes, Caledons, etc.: in some cases the shade is modified to its disadvantage, or even weakened, but in no case is it possible to obtain, by ordinary means, anything approaching a satisfactory white discharge. Some of the Indanthrene, Caledon, and Cibanone colours do, however, yield to the action of strongly alkaline Rongalite-Leucotrope discharges, and on this property is based a process for the production of white discharges on dyeings of a considerable range of extremely fast and bright grounds. Good white discharges may be obtained on dyeings of the following Indanthrenes and corresponding colours in other ranges:

Indanthrene Yellows 5 G.K., 3 G.F., G.K.;
,, Golden Yellow G.K.;
,, Brilliant Oranges G.K., R.K.;
,, Orange R.R.K.;
,, Scarlet B.;
,, Brilliant Pinks B., R.;
,, Reds B.K., R.K.;
,, Printing Purple R.;
,, ,, Violets R.F., B.F.;
,, Brilliant Violet B.B.K.;
,, Red Violets R.R.N., R.H.;
,, Blues R.K., 8 G.K.;
,, Printing Yellow G.O.K.;
,, Printing Blue R.;
,, Brilliant Green B.;
,, Olive R.;

Indanthrene Brown R.R.D.;
" Printing Browns G.N., R., 3 R.;
" Corinth R.K.;
" Grey 6 B., K.;
" Printing Black B.;
" " Blue G.G. "Suprafix;"

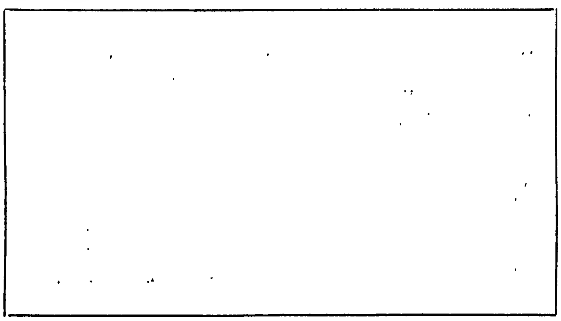
and mixtures of any of these.

The dyeing may be carried out in any of the usual ways—in the padding mangle, on the jigger, or by the continuous process described elsewhere in this work.

The dyed goods are printed with the white discharge made up as under:—

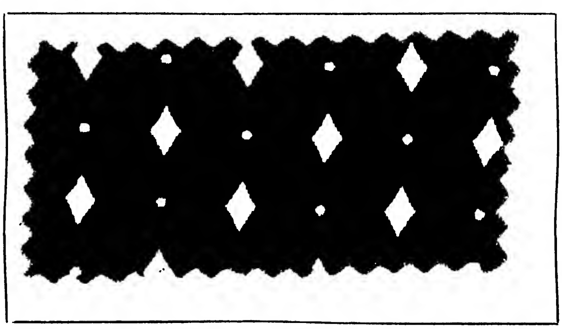
WHITE DISCHARGE:

100–100	grms.	China clay 50 per cent. paste.
150–100	"	British gum thickening 1 : 1.
225–175	"	water.
300–300	"	Rongalite C.L.
125–125	"	Leucotrope W. conc.
100–200	"	caustic soda 90° Tw.
1000	grms.	



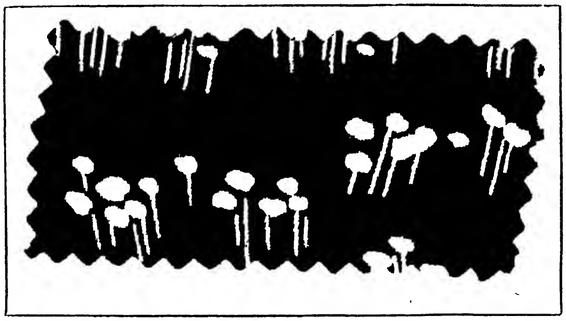
White Discharge on Indanthrene Printing Yellow G.O.K. double paste (15 per cent. dyeing) (I.G.).

After printing, the goods are steamed for 3–5 minutes in the rapid ager, cleared at the boil in dilute caustic soda (1–2 c.c. NaOH, 76° Tw., per litre), washed, soaped at the boil, washed again, and dried.



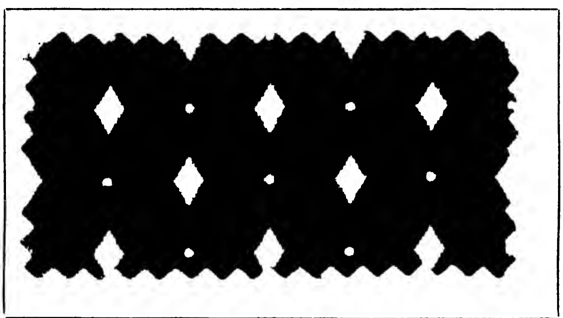
White Discharge on 20 per cent. dyeing of Indanthrene Scarlet B. paste (I.G.).

Indanthrene blue 8 G.K. yields a bright greenish-blue of good fastness, which is particularly useful for dress goods and for obtaining bright greens in combination with Indanthrene yellow 5 G.K.



Discharge on 10 per cent. dyeing of Indanthrene Blue 8 G.K. paste (I.G.).

Myrtle shades produced from mixtures of Indanthrene blue 8 G.K. and Indanthrene golden yellow G.K., and greys from Indanthrene grey K. and Indanthrene blue R.K., together with rich full blues from Indanthrene printing blue G.G. " Suprafix," are used to a considerable extent for the dyeing of cotton velvet for high-class dress and furnishing fabrics.



Discharge on 20 per cent. dyeing of Indanthrene Printing Blue G.G. "Suprafix" (I.G.).

Coloured discharges are not practicable on Anthraquinone dyestuffs of the foregoing type, but some variation may be obtained by printing a discharge white on a ground dyed with a mixture of dischargeable and undischargeable colours ; and Aniline black may also be printed along with a white discharge if suitable precautions are observed to prevent the black from working into the white, or *vice versa*, during printing.

By these various methods of discharging vat colour grounds of the Indigoid, Anthraquinone, and Indigosol groups, the effects of the old standard Indigo styles may be reproduced in a great variety both of printed and ground colours remarkable alike for fastness and brightness.

Discharging of Turkey Red.

The production of white and coloured patterns on dyed Turkey-red grounds is effected in two totally distinct ways, namely, (1) by the Acid or Chloride of Lime process, and (2) by the Glucose-Alkali process.

Both these methods are in general use, and are of the utmost practical value for the printing of the well-known "Turkey-red chintzes."

(1) **The Acid Process.**—The acid process derives its name from the fact that the dyed material is printed with strongly acid solutions, though the real discharging agent is bleaching powder, through a solution of which the cloth is passed after printing. The acids liberate hypochlorous acid from the bleaching powder, and this acid destroys the Turkey red on the printed parts of the cloth.

For a white discharge either citric, tartaric, or arsenic acid may be used with equally good effect, but for colours the organic acids only are employed. Yellow is obtained from citric acid and lead salts; blue from a solution of Prussian blue in oxalic and tartaric acids; and green from a mixture of blue and yellow. The black printed on Turkey red in the acid discharge process is generally a Logwood and iron black, which fixes itself on drying, and which is made sufficiently strong to resist the bleaching action of the bleaching powder bath. Aniline black is out of the question, since it requires either steaming or a few hours' ageing for its development, and both these processes give rise to defective work. Steaming causes the strong acids to attack and tender the fibre, and ageing gives them both the time and the chance to absorb moisture, which causes them to run, and thus give clumsy impressions with woolly edges.

After printing, the goods are carefully dried (in hot air if possible), and are then run in a continuous manner, and at the full open width, through a series of tanks or becks fitted with top and bottom guide rollers and squeezer bowls, in much the same way as an open soaper. The first of these becks contains a solution of bleaching powder 12° Tw., and a little chalk to prevent it from becoming too acid; the second and third are supplied with running water; the fourth contains a slightly warm ½–1 per cent. solution of bichromate of potash to precipitate the lead salts as Chrome yellow; and the rest consist of washing becks, through each of which fresh water flows continuously.

The object of the bleaching powder is twofold: (1) to discharge the Turkey red from the printed parts of the cloth, and (2) to precipitate the lead salts as chloride, which, being insoluble in cold water, adheres to the cloth during the following operation of washing in the second and third becks, and is finally fixed as the quite insoluble Chrome yellow in the bichromate or chrome bath.

Blue shades of Turkey red are more difficult to discharge than the yellow shades, and in practice the latter are almost invariably used, as they are both easier to manipulate and yield more brilliant effects. The bluer shades can, however, be discharged satisfactorily, and are occasionally employed for home trade chintzes. Another point to observe in the discharging of Turkey red is to avoid an excess of oily compounds on the fibre: they resist the penetration of the acid printing colours, and therefore prevent the bleaching liquor from acting anywhere but on the surface of the material, with the result that an incomplete discharge is obtained.

The various discharge colours may be made up as follows:—

Discharge White I.

{600	grms.	water.
{115	,,	flour. Boil, cool, and add whilst cooling—
250	,,	citric acid.
30	,,	oxalic acid.
5	,,	Indigo extract (for sightening).
1000		

Discharge White II.

435 grms.		water.
80	,,	acetic acid 9° Tw.
100	,,	flour. Boil, cool, and add—
380	,,	arsenic acid 175° Tw.
5	,,	Blue standard 15 per cent.
1000		

Discharge Blue I.

300 grms.		water.
25	,,	starch.
15	,,	olive oil.

Boil, cool, and add—

15 grms.		turpentine.
250	,,	Blue standard 15 per cent.
145	,,	arsenic acid 175° Tw.
300	,,	White discharge II.
1000 when cooled.		

Discharge Blue II.

450 grms.		water.
50	,,	starch.
50	,,	flour.
25	,,	olive oil. Boil, and whilst cooling add—
200	,,	tartaric acid (pulverised). Cool, and add—
250	,,	Blue standard 15 per cent.
1000 when finished.		

Blue Standard 15 per cent.

300 grms.		Prussian blue 50 per cent. paste.
50	,,	oxalic acid. Allow to stand over-night, then add—
650	,,	boiling water, and stir till dissolved.
1000		

Discharge Yellow.

350 grms.		water.
250	,,	lime juice 48° Tw.
100	,,	flour.
200	,,	lead nitrate. Boil, cool a little, and add—
100	,,	tartaric acid. Cool.
1000		

Discharge Green, 8/1.

800 grms.		Discharge yellow.
100	,,	Discharge blue I. or II.

A somewhat brighter green is obtained by replacing a portion of the lead nitrate in the yellow with lead acetate. About equal parts of each give a good result.

Print the above colours on Turkey-red dyed cloth; dry and pass through

bleaching powder solution 12° Tw.; wash and pass through a ½ per cent. solution of sodium bichromate at 30°–40° C.; wash well and dry.

If the rollers are lightly engraved or worn down, the percentage of acid will require to be increased; as a rule, however, it is better to strengthen the engraving, since the strengthened colours are apt to crystallise out.

Almost any Logwood and iron black is suitable for printing alongside the chintz colours given above. The only condition to be observed is to make it strong enough to withstand the oxidising action of the bleaching powder bath. The addition of a little Prussian blue improves the shade; the blue may be added either as such or formed in the colour during its preparation. Both the following blacks are used on the large scale:—

Black I.

475	grms.	Logwood extract 18° Tw.
32·5	,,	acetic acid 9° Tw.
225	,,	pyrolignite of iron 28° Tw.
75	,,	starch.
25	,,	British gum.
23·75	,,	nitrate of soda.
12·5	,,	olive oil. Boil, cool, and add—
37·5	,,	acetate of copper 40° Tw.
93·75	,,	nitrate of iron 54° Tw.
1000		

Black II.

12·5	litres	Logwood extract 48° Tw.
32·5	,,	water.
20	,,	acetic acid 9° Tw.
5	,,	olive oil.
10	kilos.	starch.

Boil, and add—

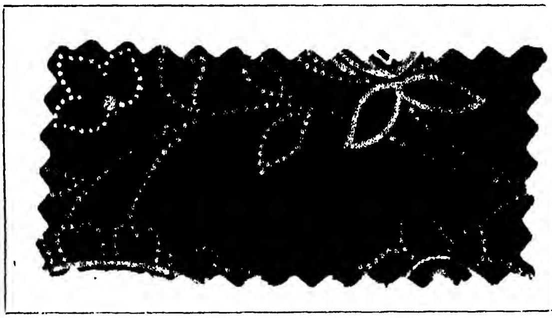
5·5	kilos.	ferrous sulphate.
10	litres	water.
2	kilos.	yellow prussiate of potash.
10	litres	water.
1·25	,,	red liquor 8° Tw., and when cold—
1·25	,,	nitric acid 60° Tw.

100 litres when finished.

Both these blacks are fixed on the fibre by the mere operation of drying after printing. Black II. after fixing contains Prussian blue.

In all the Logwood blacks used for Turkey-red chintzes the Logwood is present in the form of a finely divided precipitate, and this makes them difficult to work in the ordinary way, as they stick in the engraving. In order to prevent this as much as possible a brush furnisher must be used; and in some works a strip of wire card fixed on a bar of wood is used instead of a lint doctor. The card scratches the smooth surface of the roller considerably and wears down the engraving rapidly, but it answers its purpose admirably, and, apart from the cost of engraving, it is really an economical arrangement, since it ensures a good, full impression of the pattern (of the black roller). The black roller certainly scums badly owing to the rough state of its unengraved surface, but in reality this scum consists of so thin a

film of black that it is entirely removed in the subsequent operations, and hence it has no detrimental influence on the ultimate effect. As a matter of fact, it is owing to the energetic action of bleaching powder on Logwood that it is essential to print the cloth heavily with very strong blacks. A good part of the black is removed in the discharging beck, and if it is at all weak to



Turkey Red – Acid Discharge (F. Steiner & Co., Ltd.).

commence with, or has been printed with a worn or a too lightly engraved roller, it is quite impossible to obtain a full, rich black.

Many recipes for discharge colours are in general use, but they are based upon the same principle as, and consist of so many modifications of, those given above. The only exception of any note is the use of lactic acid, patented by C. F. Boehringer & Sons, of Nieder Ingelheim a/Rh. It is claimed by them that lactic acid possesses advantages over other organic acids, but so far it has not displaced these latter to any great extent.

(2) **The Glucose-Alkali Process. (Alkaline Discharges.)**—This process is based upon the fact that Alizarin alumina lakes (Turkey red, etc.) are soluble in concentrated caustic soda, and, when associated with the glucose process of Indigo printing, it affords an exceedingly valuable means of producing very fast Turkey-red chintz styles. Indigo is much faster than Prussian blue to soaping, and another great advantage is that Aniline black may be used, so that, taken altogether, alkaline discharges yield the most permanent colours it is possible to apply to Turkey red. As in the acid process, the discharge yellow is produced on the fibre by precipitating a lead salt with bichromate, and the green is a mixture of Indigo and Chrome yellow.

The general method of working is practically identical with the glucose process of Indigo printing. The Turkey-red dyed cloth is first prepared in a 25 per cent. solution of glucose ; then dried, printed with the alkaline colours, steamed for 2–3 minutes in the rapid ager, passed through a boiling solution of silicate of soda to clear the whites, etc., and finally passed through an acidified solution of bichromate of soda to develop the Chrome yellow and the green.

Caustic soda alone does not yield a satisfactory white, for, although it dissolves out the Alizarin lake, it always leaves a white tinged more or less strongly with pink. To obtain a pure white discharge it is necessary to add an alkaline solution of stannous chloride, silicate of soda, and a trace of Indigo to the thickened caustic soda. These additions enhance the purity of the white enormously, but are not essential in the case of blue, yellow, and green.

Alkaline Discharge White I.

$\left\{\begin{array}{l}\text{750 grms. alkaline thickening T.R.}\\ \text{100 ,, stannous chloride.}\end{array}\right.$

Mix the stannous chloride very gradually with the thickening at a temperature not exceeding 30° C. When dissolved add—

148 grms. silicate of soda 77° Tw. and—
2 ,, Indigo 20 per cent. paste.

1000

ALKALINE DISCHARGE WHITE II.

758 grms. alkaline thickening T.R.
70 ,, glycerine.
50 ,, stannous chloride.
100 ,, silicate of soda 77° Tw.
20 ,, turpentine.
2 ,, Indigo 20 per cent. paste.

1000

ALKALINE DISCHARGE YELLOW I.

625 grms. alkaline thickening T.R.
300 ,, lead hydrate 50 per cent. paste.
75 ,, silicate of soda 77° Tw.

1000

ALKALINE DISCHARGE YELLOW II.

100 grms. lead acetate.
40 ,, lead nitrate.
90 ,, boiling water.
60 ,, glycerine.

Dissolve, and add to—

675 grms. alkaline thickening T.R.
35 ,, silicate of soda 77° Tw.

1000

ALKALINE DISCHARGE BLUE.

730 grms. alkaline thickening T.R.
20 ,, starch (maize).
50 ,, water.

Heat to 60° C., cool, and add—

150 grms. Indigo 20 per cent. paste.
30 ,, glycerine.
20 ,, turpentine.

1000

ALKALINE DISCHARGE GREEN I.

560 grms. alkaline thickening T.R.
240 ,, lead hydrate 50 per cent.
100 ,, Discharge White II.
20 ,, turpentine.
80 ,, Indigo 20 per cent. paste.

1000

DISCHARGE GREEN II.

3 parts Yellow II. above.
1 part Alkaline Discharge Blue.

ALKALINE THICKENING T.R.

100 grms. light British gum.
900 ,, caustic soda 100° Tw.

1000

Heat to 60° C. and cool before use.

Any steam Aniline black or a Diphenyl black may be printed in conjunction with the alkaline discharge colours. As a rule, a strong Vanadium black is preferred, but equally good results are obtained from Copper sulphide blacks; and if the pattern is a heavy one, a Prussiate black yields perfectly satisfactory results, and is, moreover, much safer to use, since it is not nearly so liable to tender the fibre. Recipes for Aniline blacks will be found in the section on the Steam Style.

After printing, the goods are thoroughly dried, and steamed immediately in the rapid ager for 2–3 minutes. They are then passed through a boiling 2–3 per cent. solution of silicate of soda for 3–5 minutes, well washed in water, chromed in an acidified solution of bichromate of potash or soda, and finally washed well and dried. The Chrome bath is made up as follows:—

CHROME BATH ½ per cent.

100 litres water.
500 grms. sulphuric acid 168° Tw.
500 ,, bichromate of potash.

Used at 30°–40° C.

In order to secure the best results, the following precautions must be observed after printing:—

(1) The goods must be quite dry before steaming, otherwise the colours will run and the discharge will be imperfect.

(2) Steaming must be proceeded with as soon as possible after printing. If the printed goods are allowed to lie, the colours absorb carbonic acid from the air; and as sodium carbonate is quite useless as a discharging agent, the results are poorer the longer the goods remain unsteamed.

(3) In chroming, care must be taken to avoid using too strong a bath, lest the blue be impoverished by too energetic an oxidation. In cases where the pattern contains very light blues, the amount of sulphuric acid may be reduced, and sometimes even it is advisable to omit it entirely.

A modification of the alkaline discharge process consists in first printing the glucose-prepared Turkey-red cloth with white, blue, green, or yellow, and then, after drying, printing it with a cover pattern in Aniline black. The alkalinity of the discharge colours prevents the development of the black during the steaming process, so that a clear-cut coloured pattern appears on a figured ground of black and red. This style is chiefly confined to black, red, and yellow effects.

One of the most important uses of the Glucose-alkali discharge is in the production of the well-known Blue and Red Style. This consists for the most part of Indigo-blue stripes and blotches on a Turkey-red ground, and is produced by methods identical with those already described. A simpler and quicker method of obtaining the same effect is, print a mixture of Indigo, caustic soda, and hydrosulphite on plain *unprepared* Turkey-red cloth. For this purpose the following colour may be used:—

INDIGO BLUE H.S.

700	grms.	alkaline thickening T.R.
{75	,,	hydrosulphite N.F. conc.
{75	,,	water.
150	,,	Indigo 20 per cent. paste.
1000		

Print; dry; steam 2–3 minutes in air-free steam at 102° C.; pass through 1 per cent. solution of silicate of soda, wash well in water and dry.

The Anthraquinone and Indigoid vat blues are both suitable for Turkey-red discharge styles by the alkaline process, and neither requires the cloth to be previously prepared with glucose, although somewhat better results are obtained if glucose is used. Both classes of blue are far faster than Indigo in every respect, and, so far as shade is concerned, they are much brighter and purer in tone. It is surprising that their application to Turkey-red chintz styles has been almost ignored, and that they are practically unused for Turkey-red discharges on the large scale. It is therefore impossible to say how they would work in bulk; but judging from the results obtained in the laboratory from the colours given below, it would appear that they have a future before them in this branch of the industry.

CIBA BLUE DISCHARGE ON TURKEY RED.

{120	grms.	Ciba blue 2 B.D. paste.
{40	,,	stannous hydrate 50 per cent. paste.
{50	,,	glycerine.
40	,,	gum Senegal 30 per cent.
750	,,	alkaline thickening T.R.
1000		

Allow to stand ½ hour before using.

Ciba violet B. or R. may be used in the same way.

INDANTHRENE BLUE DISCHARGE ON TURKEY RED.

150	grms.	Indanthrene blue R.S. paste.
60	,,	stannous hydrate 50 per cent. paste.
50	,,	glycerine.
740	,,	alkaline thickening T.R.
1000		

Allow to stand 1–2 hours before printing.

Indanthrene yellows, oranges, and green are also suitable.

After printing either of the above classes of colours, the goods are well dried and steamed 4–5 minutes in air-free but slightly moist steam at 100°–102° C. They are then rinsed in cold water for a few minutes, run through boiling silicate of soda, chromed for the lead yellows, and finally well washed and soaped to brighten the shades.

Other vat dyestuffs can be applied in an analogous manner.

The Discharging of the Insoluble Azoic Colours.

The problem of producing discharge effects on cloth dyed with the insoluble Azoic colours has long occupied the attention of chemists, and has only been solved satisfactorily since the introduction of the hydrosulphite-formaldehyde compounds.

The insoluble Azoic colours are destroyed by powerful reducing agents, and

the earlier methods of discharging them were based upon the well-known reducing properties of stannous oxide and of glucose-alkali. Stannous oxide alone has not much action on Azoic colours produced on the fibre, but H. Schmid, in 1896, succeeded in discharging them to a pure white by adding certain organic solvents to the tin oxide paste. In this connection the use of acetin was patented by the Farbwerke Höchst, and tin oxide discharge colours were put on the market under the names of—

Discharge white P.N.	Discharge yellow P.N.
,, blue P.N.	,, green P.N.

These, thickened with starch and British gum, were printed on cloth dyed with colours prepared from para- and meta-nitranilines, nitrotoluidine, amino-azo-benzene, nitrophenetidine, and β-naphthylamine.

The printed goods, well dried, were steamed for 5–8 minutes in air-free steam at 100° C., and if printed in white only, were then well washed, soured in hydrochloric acid $1\frac{1}{2}$° Tw., washed again, and passed through a weak solution of bleaching powder, which increased the brilliancy of the white and improved the brightness of the red or orange ground colour.

For blue discharges and Aniline black, the goods, after steaming, were treated successively in the following solutions, through which they passed continuously at the full open width :—

(1) For $\frac{1}{2}$ minute through hydrochloric acid 1° Tw. at 60° C.
(2) Cold water.
(3) Warm $\frac{1}{2}$ per cent. solution of bichromate of potash in hydrochloric acid 1° Tw. at 60° C.
(4) Hydrochloric acid 1° Tw. at 60° C. for 1 minute.
(5) Well washed in water and dried.

For yellow and green discharges, in combination with black, white, and blue, the goods were simply treated in a solution of tartar emetic, followed by a thorough washing in cold running water to re-oxidise the reduced blue and green dyestuffs. The addition of a little peroxide of hydrogen accelerates the oxidation, but neither bleaching powder nor chrome is to be recommended, as they destroy the yellow.

The colours being the tin lakes of basic dyestuffs, are *not* remarkable for their fastness to soap.

The glucose-alkali discharge is carried out in the same way as for Turkey reds, except that the printed goods are treated in a slightly different manner after steaming. Instead of being run through a boiling solution of silicate of soda, they are passed through tepid sulphuric acid at 8° Tw., then washed, soaped, and washed again. If yellow and green are printed, the goods are finally chromed as usual in an acidified chrome bath, washed well and dried.

The ordinary alkaline discharge blue, yellow, and green as used for Turkey red may be employed for the insoluble Azoic reds and oranges. The addition of 17–18 per cent. of glycerine is, however, essential to the securing of the most perfect discharges. The colours are very fast, and in this respect the glucose-alkali discharge is superior to the tin oxide process.

Neither method is, however, applicable to colours prepared from α-naphthylamine, tolidine, benzidine, or dianisidine, none of which can be satisfactorily discharged by any practicable reducing agents except the sulphoxylate compounds (hydrosulphites).

The tin oxide process of H. Schmid and the alkali-glucose process of Schlæpfer, Wenner & Co. are therefore limited to the discharging of red and orange ground colours only. Moreover, both processes together only include

the application of a very small number of dyestuffs, so that, on the whole, it is not surprising that they have been superseded by the hydrosulphite process, which is not merely applicable to almost every insoluble Azoic colour, but which is much simpler and safer, reliable and successful in practice, and is adaptable to the production of coloured discharges in Basic, Sulphur, Mordant, Pigment, and vat dyestuffs.

The Hydrosulphite Process.—The first hydrosulphite preparations which appeared on the market were of little practical value for any kind of calico printing on account of their instability; and an insoluble zinc preparation, Hydrosulphite Z., was of scarcely greater use, because, although it was fairly stable, it was exceedingly difficult to print, by reason of the fact that even with a brush furnisher it persistently stuck in the engraving. The discovery of the stable and very soluble hydrosulphite-formaldehyde compounds by Baumann, Thesmar, and Frossard, chemists at Zündel's Works in Moscow, was an important event in the history of calico printing, and has rendered easy the production of discharge effects on insoluble Azoic colours—effects altogether novel, and otherwise impossible of attainment.

Thickened solutions of these compounds printed on Para red and Para brown give, on steaming, remarkably pure white discharges. For coloured effects, any dyestuffs which resist the powerful reducing action of the hydrosulphites, and which, at the same time, are capable of being fixed by a process of steaming, are suitable. Of these, certain Basic colours are the most important, but others, such as the vat dyes, Gallocyanine and Modern violet groups, and the Sulphur colours, are coming more and more into use for fast dark styles.

α-Naphthylamine clarets and Benzidine and Tolidine puces are only discharged by prolonged steaming at a high temperature, such as is obtained in the Simon-Weckerlin apparatus. But by adding certain catalytic agents to the discharge paste, it is possible to produce perfect discharges on these colours in the ordinary hydrosulphite ager at a temperature of 102° C. The firm of Meister, Lucius & Brüning observed that the presence of certain compounds derived from the action of formaldehyde on xylidine and other amines had the effect of rendering Naphthylamine clarets capable of being discharged by the usual methods of steaming.

In 1905 they put on the market a product of this kind under the name of Rodogen. Rodogen could be added either to the printing colour, or the cloth could be prepared in a weak solution of it and then printed with the same discharges as were used for Para red. Both methods gave equally good results, the latter being generally preferred, as it allowed of one set of colours being used for different ground colours. The only objection to it is, that the shade of claret is dulled slightly.

About the same time Wilhelm found that certain colouring matters—Setopaline, Alizarin orange, Acridine yellow, Rhodamine—increased the dischargeability of Naphthylamine clarets, and a little later (Feb. 1906) the Badische Co. patented a process for the same purpose—a process so simple, elegant, and perfect that it almost immediately displaced all other methods then in use. The Badische Co.'s patent claimed the use of Induline scarlet, of which one-third of a grm. per kilo. of a 20 per cent. hydrosulphite discharge paste is quite sufficient to produce a fine white on claret and chocolate grounds.

Another method, used with great success in practice, was discovered by Sunder, and described by him in the *Bulletin de la Société Industrielle de Mulhouse*. Sunder's method consists in adding a small quantity of anthraquinone to the discharge colours, and while it yields results equal to those obtained by the Badische Co.'s process, it has a slight advantage over the latter,

inasmuch as in large patterns the white is entirely free from the faint pinkish tinge imparted by the Induline scarlet. On the other hand, Induline scarlet can be applied in two ways like Rodogen, whereas anthraquinone being insoluble can only be mixed with the printing colour in the form of a finely ground paste. The quantity of anthraquinone required to produce a pure white is from 7 to 10 grms. per kilo. of printing colour.

The two processes of the Badische Co. and Sunder have superseded those of Baumann and Thesmar (iron salts and nitrite), Meister, Lucius & Brüning (Rodogen), and Wilhelm (Setopaline, etc.) in most printworks, and may be regarded as the most important up to date.

The pinkish appearance of large patterns discharged by the Induline scarlet method may be avoided by using Patent blue in place of the scarlet. In this case 20–30 times more dyestuff must be used, but the discharge takes place more rapidly.

Oxidising agents printed on Para red, Naphthylamine claret, etc., preserve them from being discharged, by counteracting the reducing action of the hydrosulphite discharge cover patterns afterwards printed over them. On red and claret the resists consist of citric or tartaric acid, with chlorate of soda under white covers, and of the same substances with antimony salts under basic colours. On Para brown an alkaline solution of copper gives the best results under white discharges. Recipes for these and other resists will be given later.

Previous to the outbreak of war, practically all the hydrosulphite-formaldehyde preparations used in this country were supplied from Germany, or by German firms established here. Since 1914, however, English and American firms have succeeded in manufacturing in bulk, products that are as good as any that ever came from the Continent, and, at present, their output is sufficient to fulfil all our requirements. Several of the special hydrosulphites, containing catalysts (Induline scarlet, etc.) and Leucotrope W., were never more than conveniences, and many important firms never used them, preferring to work with formulæ of their own devising and of known composition. For the discharging of Naphthylamine clarets, Induline scarlet and Rodogen are now rarely used, their place being taken by anthraquinone; and such preparations as Rongalite C.L. are easily replaced by mixtures of sulphoxylate-formaldehyde and Metabol (a Leucotrope W. made by the Imperial Chemical Industries, Ltd.).

It is not likely that German hydrosulphites will ever again attain their old importance in the British market; but as they are again being offered here, it is necessary, for purposes of comparison, to include them in the following list of the more important of such products:—

(1) Formosul (Brotherton).
(2) Hydrosulphite A.F.C. (A. Ashworth).
(3) Britulite.
(4) Hydrosulphite N.F. (conc.).
(5) Rongalite C.
(6) Hyraldite C. extra.
(7) Rongalite C. special.
(8) Hydrosulphite N.F. special.
(9) Hyraldite A. special.
(10) Rongalite C.L.
(11) Hydrosulphite C.L.
(12) Hyraldite C.L.
(4)–(12): (I.G.).

The first six products consist essentially of the formaldehyde compound of sodium sulphoxylate ($NaHSO_2.CH_2O+2H_2O$), of which they contain from

75–88 per cent. So far as their respective reducing powers are concerned there is little to choose between them; all are equally effective, and may replace each other, weight for weight, in any of the recipes given hereafter. Nos. 7, 8, and 9 consist also of sulphoxylate-formaldehyde, but contain, in addition, the requisite quantity of catalytic agents which are necessary for the discharging of Naphthylamine clarets and Benzidine and Tolidine chocolates. The last three compounds (Nos. 10, 11, and 12) are mixtures of hydrosulphite-formaldehyde and Leucotrope W.; they find their particular application in the discharging of Indigo, and are only noted here *en passant*. Mixtures of Nos. 1, 2, and 3 with Anthraquinone or Metabol, according to circumstances, replace perfectly the last six special products. The general name for all sodium sulphoxylate-formaldehyde compounds is Hydrosulphite, though, strictly speaking, this term is incorrect since hydrosulphites are really salts of an acid having the formula $H_2S_2O_4$, whereas the "hydrosulphites" mentioned above correspond to sulphoxylic acid, H_2SO_2.

Formosul, Britulite, and Hydrosulphite A.F.C. have all been used interchangeably by one of the authors during the last few years in the production of large quantities of Indigo prints and Azoic-colour discharges. The high quality of the results obtained is sufficient proof of the excellence of these British products.

Basic colour discharges contain, in addition to the dyestuff, hydrosulphite and tannin, certain organic substances—*e.g.* aniline, phenol, acetin, alcohol, glycerine, etc.—not merely to prevent the too rapid precipitation of the colour lake, but also to influence favourably the brightness, keeping qualities, and regular working of the colours. Mordant colours of the Gallocyanine and Modern violet group are made up as for the steam style, but with the addition of a sufficient quantity of hydrosulphite to discharge the dyed Azoic colour grounds; and the same may be said, in the main, of the Vat dyestuffs, Sulphur colours, and Pigment colours. Any important variation from type will be found by an inspection of the formulæ given in the following.

(*a*) Discharges on Paranitraniline Red, Para Brown, and Nitro-toluidine and m-Nitraniline Oranges.

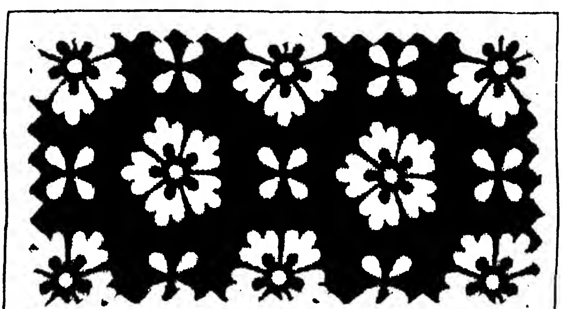
Discharge White P.

250	grms.	Rongalite C. (or Formosul).
50	,,	glycerine (optional).
250	,,	British gum paste.

Dissolve at 50°–60° C., and add to—

450 grms. starch-tragacanth paste,

1000



Paranitraniline Red discharged with Formosul (I.C.I.).

Discharge White II. P.

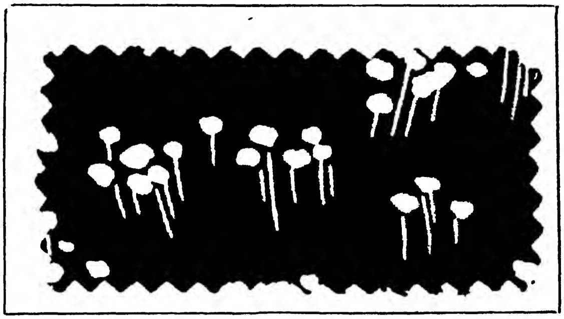
225 grms. Rongalite C.
200 ,, British gum paste.

Dissolve at 50° C., cool, and add—

10 grms. formaldehyde 40 per cent.
10 ,, hydrochloric acid 33° Tw.
50 ,, water.
505 ,, starch-tragacanth paste.

1000

Discharge White II. P. is especially suitable for Para browns, but White I. is almost equally effective, though the goods require a more complete washing. For flannelettes and other rough cloths it is advantageous to add zinc oxide to both the above discharges. Zinc oxide acts mechanically, preventing the undue absorption of the discharge by the material, and simultaneously improving the white by forming a white covering over the fibres. With a sufficiently strong discharge, however, and a heavily engraved pattern, the use of zinc oxide is unnecessary, and its absence improves the working qualities of the colours.



Para Brown (Brown Salt R.) discharged with Rongalite C. (I.G.).

(1) Basic Colour Discharges.—The fastest colours are obtained with a starch-tragacanth thickening; gum Senegal gives more level shades in large patterns, and can be used for such, but it gives colours which lose a good deal of depth in washing, and should therefore be avoided as much as possible. In a slightly less degree, the same remarks apply to British gums.

Among the Basic colours which withstand the reducing influence of hydrosulphites, the following are, perhaps, the most generally employed:—Auramine, Thioflavine T., Rhodamine 6 G. extra, Thionine blue O. or G.O., Acridine orange D.H., Flavophosphine R. conc., and Fast Marine blue S. extra.

	Yellow P.	Pink P.	Blue P.	Orange P.	Green P.	Dk. Blue P.
Auramine conc.	..	..	..	..	15	..
Thioflavine T.	20	..	..	16	..	..
Rhodamine 6 G. extra	..	10	..	4	..	..
Thionine blue O.	..	..	25	..	5	..
Fast marine blue S. extra.	..	..	..	..	..	30
Glycerin	40	40	35	40	40	30
Alcohol	40	40	40	40	40	40
Water	100	100	100	100	100	100
Starch-tragacanth paste	200	210	200	200	200	200
Tannic acid solution 50 per cent.	100	100	100	100	100	100
Discharge paste C.D.	500	500	500	500	500	500
	1000	1000	1000	1000	1000	1000

DISCHARGE PASTE C.D.

20	grms.	starch.
90	,,	water.
400	,,	4 per cent. gum tragacanth.
90	,,	aniline oil.

Boil, cool to 60° C., and add—

400 grms. Formosul.

Dissolve at 60° C. and maintain at this temperature until the aniline is thoroughly incorporated. Properly made, the paste ought to be homogeneous and of a light yellow colour, and almost as transparent as gum-tragacanth thickening.

If desired, the aniline may be replaced by 100 grms. phenol; and acetin may be used instead of alcohol.

Some Rhodamine pinks require to be exposed to the air for a considerable time before they re-oxidise to their full shade; and as this is a tedious operation, they are often replaced by the bright but more fugitive Phthaleïn colours, fixed with chromium acetate. Thus:—

DISCHARGE PINK.

40	grms.	Erythrosine A. (or Eosin or Phloxin).
50	,,	glycerine.
60	,,	starch.
350	,,	water.

Boil, cool, and add—

100	grms.	chromium acetate 32° Tw.
200	,,	Formosul or Britulite.
200	,,	4 per cent. tragacanth thickening.
1000		

The Phthaleïn pinks are by no means so permanent as Rhodamine (or Irisamine), but they are very bright, pure colours, and require no special treatment for their development after steaming.

(2) MORDANT COLOUR DISCHARGES.—The application of the mordant colours to the production of discharge effects on Para red, etc., is confined almost exclusively to the printing of dark blues, obtained from Modern violet and Modern blue (Durand and Huguenin), Chrome violet blue (Geigy), and the lighter blue, Chromoglaucine (I.G.). Other dyestuffs of the Gallocyanine group may also be employed.

The Phthaleïn colours already given are also, in a sense, mordant colours when fixed with chromium acetate, though, as a rule, they are not included in this category.

NAVY BLUE C.V.I.

30	grms.	Modern blue C.V.I.
80	,,	acetic acid 9° Tw.
20	,,	acetin.
265	,,	water.
75	,,	starch.
200	,,	5 per cent. tragacanth thickening.
30	,,	olive oil.

Boil, cool, and add—

100	grms.	chromium acetate 30° Tw.
300	,,	discharge paste R. 60 per cent.
1000 when finished.		

Navy Blue C.G.

50	grms.	Chromoglaucine V.M. 40 per cent. paste.
200	,,	water.
150	,,	starch paste 20 per cent.
200	,,	6 per cent. tragacanth thickening.
100	,,	chromium acetate 30° Tw.
300	,,	discharge paste R. 60 per cent.
1000		

Discharge Paste R. 60 per cent.

600	grms.	Formosul or other sulphoxylate-formaldehyde.
400	,,	6 per cent. tragacanth thickening.
1000		

Blue 1900 and Modern violet 40 per cent. paste may be applied like Navy blue C.V.I. and Navy blue C.G. respectively. The addition of tannin is beneficial in both cases, inasmuch as it increases the fastness of the colour, and gives it a bluer tone than can be obtained from the chrome lake alone.

The mordant-blue discharges find their chief use in the production of the well-known and popular Blue and Red style, which was formerly produced either by the alkaline Indigo discharge on Turkey- and Para-reds, or by tannin resists under the latter.

(3) Albumen Discharge Colours.—The albumen discharge colours are of secondary importance, and are only used occasionally. The pigments used consist for the most part of the tannin lakes of the basic colours: the most important pigment colour—Lead or Chrome yellow—is unreliable, since it is apt to be destroyed by the hydrosulphite in steaming; and although it sometimes withstands the reducing action, it is not to be depended upon. The other ordinary pigment colours are either more or less affected in the same way or they offer no advantages over the tannin lakes.

The tannin lakes are prepared by precipitating a mixed solution of dyestuff and tartar emetic with a solution of tannin. The precipitate is washed well with water and then filtered to a consistency corresponding to 50 grammes of the original dyestuff per kilogramme of paste.

The printing colours are prepared as follows:—

	Yellow.	Green.	Blue.
Thionine blue G.O. lake	..	100	400
Thioflavine T. lake	400	300	..
Starch-tragacanth thickening	150	150	150
Blood or egg albumen 50 per cent. solution	150	150	150
Discharge paste R. 60 per cent. (see above)	300	300	300
	1000	1000	1000

Treatment of the Goods after Printing.—After printing, the pieces are well but not too hardly dried, and then steamed for 2–3 minutes in the hydrosulphite ager at 102°–103° C. They are then allowed to lie exposed to the action of the air for a short time in order to re-oxidise the leuco compounds

of the colouring matters, and finally fixed, washed, and soaped. Tannin colours are run through 1–2 per cent. solution of tartar emetic, and, when associated with mordant blues, are further passed through a chrome bath, which promotes the re-oxidation of all leuco compounds. The fixing in tartar emetic, the chroming, and the subsequent washing, soaping, and drying are all done in the open width, and, as a rule, in a continuous manner. In this way all chance of the colours marking off is avoided.

(4) Vat and Sulphur Colours on Paranitraniline Red, etc.—The composition of vat and Sulphur colour discharges on insoluble Azoic colour grounds differs only from that of the ordinary printing colours in that the quantity of hydrosulphite is increased sufficiently to discharge the dyed grounds. As was foreshadowed in the first edition of this work, these two classes of colours are now largely employed for all classes of discharge work; and it is not unlikely that both groups will, in the future, find a still wider application, the tendency being for fast discharge styles to displace blotch printing.

The following recipes are typical of the way in which these colours are made up for discharging Paranitraniline red, Para brown, and other grounds destroyed by sulphoxylates:—

Indigo Blue Discharge.

150 grms. sulphoxylate-formaldehyde.
125 „ water.

Dissolve at 50° C., and add to—

575 grms. alkaline thickening (for Indigo).

Cool and add—

150 „ Indigo 20 per cent. paste.

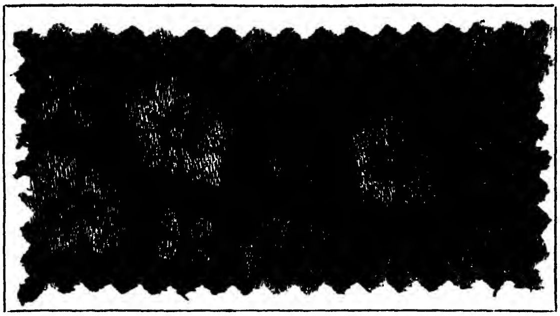
1000

Brom-Indigo may be applied in the same manner; it gives a redder shade than either natural or synthetic Indigo. Lighter shades may be obtained by reducing the proportion of Indigo.

Indanthrene Colour Discharges.

	Blue.	Yellow.	Green.
Indanthrene blue G.C.D. paste	100	..	40
„ yellow G. paste	..	100	60
Glycerin	75	75	75
Zinc oxide 50 per cent. paste	100	100	100
Water	50	50	50
British gum thickening	360	360	360
Rongalite C.	190	190	190
Caustic soda 91° Tw.	50	50	50
Potassium carbonate	75	75	75
	1000	1000	1000

The Cibanone or Caledon series may be employed instead of the above with equally good results.



Caledon Yellow R. discharge on Para Red (I.C.I.).

CIBA COLOUR DISCHARGES.

	BLUE.	VIOLET.
Ciba blue 2 B.D. paste or Durindone blue 4 B.	250	..
Ciba violet B. or R. paste	..	250
Gum Senegal 40 per cent.	120	120
British gum-paste thickening	190	190
China clay 50 per cent. paste	90	90
Glycerin	50	50
Soda ash	100	100
Hydrosulphite N.F. conc.	200	200
	1000	1000

The hydrosulphite is added last at 50° C., and then the whole is well stirred until complete solution ensues. The Ciba colours may be toned as desired by mixing them with any dyestuff which can be fixed as a leuco compound (Indigo and the Sulphide and Indanthrene colours, for example), and by this means it is possible to obtain a variety of extremely fast discharge effects.

SULPHUR COLOUR DISCHARGES.—Most of the Sulphur colours now on the market are more or less capable of yielding satisfactory discharge effects on the insoluble Azoic dyes. The Pyrogene, Kyrogene, Thiogene, and Immedial colours, etc., are all suitable for the purpose, but perhaps the most extensively employed are the two specially prepared brands of the I.G. Farbenindustrie, namely, the D. brands of the Thiogene colours and the "Immedial colours soluble." Both these groups are quite soluble in caustic soda without the addition of sodium sulphide, and their introduction has considerably simplified, and rendered more certain the results of, all processes connected with the application of the Sulphur colours.

The following directions may be observed in the preparation of colour-discharges on Paranitraniline red, etc.

SULPHUR BLUE DISCHARGE.

40 grms. Thiogene blue B.D. conc.
50 „ glycerine.
50 „ caustic soda 100° Tw.
100 „ China clay 50 per cent. paste.
270 „ British gum-starch thickening.
150 „ sulphoxylate-formaldehyde.

Heat to 50° C., cool, and add gradually—

340 grms. caustic soda 77° Tw.

1000

BRITISH GUM-STARCH THICKENING.

100 grms. maize starch.
200 „ British gum.
700 „ water.

1000

Boil and cool.

Other purified Sulphur colours are prepared for discharge work in a similar manner.

IMMEDIAL COLOUR DISCHARGE.

40 grms. Immedial colour (soluble).
20 „ caustic soda 77° Tw.
50 „ glycerine.
100 „ water.
140 „ British gum-starch paste (above).

Heat to 50° C., cool, and add—

150 grms. alkaline thickening (see Indigo printing).
500 „ Hyraldite thickening 50 per cent.

1000

HYRALDITE THICKENING 50 per cent.

500 grms. Hyraldite C. extra.
500 „ British gum paste.

The above will serve as a type of all Immedial colour discharges equal in strength and suitable for the style.

After printing Indanthrene, Ciba, and Sulphur colours, and also Indigo on Paranitraniline red, etc., the goods are dried well, steamed 2–3 minutes at 102° C., allowed to air, and then washed well in the open width. A run through a dilute solution of bichromate of potash is beneficial in re-oxidising the reduced dyestuffs, and a treatment in dilute hydrochloric acid improves the brightness of Indigo and other vat colours. The goods are finally washed again, soaped, washed, and dried.

(*b*) Discharges on H. Schmid's Bistre.

We owe to Henri Schmid an elegant process for obtaining white and coloured discharges (including a fine red) on a bistre or chocolate ground, resulting from the superposition of Aniline black on Paranitraniline red. The red-dyed cloth is first padded in a weak Aniline black, then gently dried to prevent the oxidation of the aniline, and finally printed in the discharge colours. The red is obtained by printing a substance—acetate of soda—which prevents the development of the black during the steaming operation, but which has no effect upon the red itself. The other colours and the white must, of course, resist the black, and simultaneously discharge the red beneath it. For this purpose the Basic colour discharges given on p. 631 are used with the addition of 120–150 grammes acetate of soda per kilogramme of printing colour. The red and white discharges are prepared as follows :—

WHITE DISCHARGE S.B.

250 grms. Formosul.
600 „ 6 per cent. tragacanth thickening.

Dissolve at 50°–60° C., cool, and add—

150 grms. acetate of soda.

1000

Red Resist S.B.

	I.	II.
Sodium acetate (crystals)	150	100
Sulphite of potassium 90° Tw.	..	125
Gum Senegal 30 per cent. (or tragacanth)	850	775
	1000	1000

No. II. gives the brighter red.

The bistre or chocolate ground to be discharged is obtained by padding Paranitraniline-red dyed cloth in the weak Aniline black given below :—

Black for Bistre.

I. { 75 grms. aniline salt.
1000 ,, water.
II. { 35 ,, chlorate of soda.
750 ,, water.
III. { 40 ,, yellow prussiate of potash.
1000 ,, water.

Mix solutions I., II., and III. when cold, and make the whole to $3\frac{1}{2}$ litres with water. Pad the red cloth in this solution, dry it gently in hot air, and then print on the discharge colours. After steaming, the goods are passed in succession through tartar emetic, water, chrome, water, soap and water, and then dried.

Another method of obtaining similar results is based upon the fact that ferrocyanide of zinc fixes Basic colours. In this instance the colours are mixed with zinc oxide and hydrosulphite, and the Aniline black contains an excess of yellow prussiate. The zinc oxide plays the double rôle of a resist for the black and a fixative for the colours.

Zinc Oxide-Hydrosulphite Resist Discharges on Henri Schmid's Bistre.

	Blue Z.	Yellow Z.	Green Z.
Thionine blue G.O.	30	..	7·5
Thioflavine T.	..	30	22·5
Glycerin	60	60	60
British gum paste	210	210	210
Dissolve, cool, and add—			
Hydrosulphite paste F.	700	700	700
	1000	1000	1000

Hydrosulphite Paste F.

{80 grms. zinc oxide.
90 ,, British gum powder.

Beat well into a creamy paste with—

280 grms. water.

Boil, cool to 50°–60° C., and add—

250 grms. hydrosulphite-formaldehyde.

700

For heavy patterns the amount of hydrosulphite may be reduced to 175 grms. For these colours the quantity of yellow prussiate in the black may be increased to 40 grms. per litre with advantage.

Print the above Blue Z., Yellow Z., and Green Z., together with White S.B. and Red resist S.B., on the bistre ground; steam 2–3 minutes at 102° C. in air-free steam, and pass through a weak chrome bath at 50° C.; wash well and dry.

This process yields very bright discharge effects on a fine chocolate ground. The red is exceedingly rich and brilliant, and is far superior to the red obtained by any other means. The zinc oxide colours are more brilliant than the tannin colours with aniline or phenol, but they are not so fast to soaping, although sufficiently so for most styles.

(c) Discharge Effects on α-Naphthylamine Claret and Benzidine and Tolidine Chocolates.

The production of white and coloured discharges on dyeings of the above three colours, and especially on the most important of them—α-Naphthylamine claret—has occupied the attention of colour chemists ever since the successful discharging of Paranitraniline red was accomplished.

The Stannous Oxide and Glucose-Alkali processes are absolutely useless for the purpose; and, as previously noted, even the strongest hydrosulphite mixtures give only an imperfect or half-discharge on α-Naphthylamine claret, except at the high temperature (130° C.) of the Simon-Weckerlin rapid ageing apparatus. Where the ordinary hydrosulphite ager (temp. 102°–104° C.) is employed, white and indeed good coloured discharges can only be obtained by the addition of Induline scarlet, Anthraquinone, Patent blue, Setopaline, etc., to the hydrosulphite discharge paste. In the absence of these and similar substances (which act catalytically), it is impossible to obtain satisfactory results under ordinary conditions; and even with Setopaline, Patent blue, and Induline scarlet, the whites are apt to be somewhat impure, owing to the re-oxidation of these colours. To some extent this defect can be overcome by a thoroughly drastic steaming, followed by the immediate soaping of the goods; and for white discharges alone, a run through acidulated bleaching powder solution cleans up the whites perfectly. Coloured discharges, however, will not stand the clearing operation, and therefore the goods should be well soaped as soon as possible after steaming. Anthraquinone, being almost colourless, is not liable to sully the whites; and although a much larger quantity of it is required than of Induline scarlet to obtain the same results, its employment does away with a strong soaping, and consequently allows of some economy being effected in the cost of dyestuffs; for the colours of patterns that have to be heavily soaped must be made darker than is otherwise necessary, in order to allow for loss of depth in process. On the other hand, the actual soiling of the whites with Induline scarlet at the strength used is so slight as to be unnoticeable in all but the largest designs; and as it is extremely reliable in work, and can be applied either in the naphthol prepare, the diazo solution, the printing colour, or to the dyed material directly by padding, it is, on the whole, the most useful addition to employ, as it is certainly the most convenient. The impregnation of the fabric during dyeing or after dyeing has the advantage over the addition to the printing colour, in that the same range of colours can then be used indiscriminately for Paranitraniline red, Para brown, Naphthylamine claret, Tolidine puce, etc. The simplest method is to add the requisite quantity of Induline scarlet (0·25–0·5 grm. per litre) to either the naphthol prepare or to the diazo solution, and dye in the usual way. The dyed goods are then soaped to render the discharging somewhat easier, and, if desired, they may also be brightened by a previous souring to remove

the excess of diazo solution, which, if allowed to remain, turns brown and dulls the shade, besides increasing its resistance to the discharge paste. Neither soaping nor souring affects the Induline scarlet prepared pieces.

The duration of the steaming operation is an important factor in the discharging of Naphthylamine claret, and indeed of all insoluble Azoic dyes. If the speed of the printed goods is so regulated that they occupy from five to six minutes in passing through the ager at 102° C., or if they are steamed twice, it is possible to obtain good whites on claret with reduced quantities of both Induline scarlet and hydrosulphite; in fact, an excellent white has been obtained in this way by printing a paste containing only 120 grammes of hydrosulphite per kilogramme on cloth dyed in a diazo solution containing as little as 0·25 gramme of Induline scarlet per litre. As a rule, however, it is inconvenient to prolong the steaming, and consequently about double the above quantities of scarlet and hydrosulphite are used for the finer patterns usually employed in discharge work on deep clarets. For ordinary shades of claret dyed like Paranitraniline red, on a 2½ per cent. naphthol prepare, but containing Induline scarlet, a satisfactory white is given with rather more than half the quantity of hydrosulphite required to obtain comparable results on the red.

In general, however, all risk of an imperfect discharge is avoided by using discharge pastes containing from 20–25 per cent. of their weight of hydrosulphite-formaldehyde compounds. The further addition of ammonium oxalate has a beneficial influence on the effectiveness of the discharge; it dissociates in steaming, and the liberated oxalic acid supplements the action of the steam in decomposing the hydrosulphite.

(1) Discharges on α-Naphthylamine Claret dyed with the addition of 0·5 grm. Induline Scarlet per litre of the Diazo Solution or of the Naphthol Prepare.

On cloth prepared and dyed by this method, discharge effects are easily obtained by printing the same colours as are used for Paranitraniline red and Para brown. The same applies to other difficultly dischargeable Azoic colours prepared in the same way. No modification of the printing colours is required, and therefore pieces dyed in red, brown, chocolate, orange, and puce can all be wound on one roll, and printed in succession without intermission, and without the loss of time occasioned by the emptying out and washing up of half a dozen colour boxes and rollers, and perhaps a dozen doctors. A white discharge which has given excellent results on claret in practice is made up as follows:—

White N.F.O.

$\left\{\begin{array}{l}\text{250 grms. hydrosulphite-formaldehyde.}\\ \text{700 ,, British gum-starch paste.}\end{array}\right.$

Dissolve at 60° C., cool, and add—

50 grms. oxalate of ammonia 5° Tw.

1000

Print white and colours (and if a black is required, a prussiate Aniline black or a Logwood-iron black); dry and steam 2–3 minutes in air-free steam at 102° C.; pass through a 1–2 per cent. solution of tartar emetic; wash well, and pass through a cold ½ per cent. solution of bichromate of soda; wash, soap, wash, and dry.

Rodogen may be used instead of Induline scarlet, but is by no means so efficient.

(2) Discharges on α-Naphthylamine Claret, etc., with the addition of the Catalysts to the Printing Colours.

In operating by this method the cloth is dyed exactly as described under insoluble Azoic colour styles, and the substances that are necessary to effect the discharge are all contained in the various printing pastes. In general, only three catalytic agents are used, namely, Induline scarlet, Anthraquinone, and Patent blue.

(a) Discharges with Induline Scarlet.

White Discharge I.N.

250 grms. hydrosulphite-formaldehyde.
50 ,, glycerine.
350 ,, 5 per cent. tragacanth thickening.

Dissolve at 60° C. and add—

320 grms. starch paste.
30 ,, 1 per cent. solution of Induline scarlet.

1000

Heat gently until the scarlet is reduced.

Hydrosulphite N.F. conc. special, or the corresponding Hyraldite A. special, or Rongalite C. special, may all be used instead of the ordinary formaldehyde compounds of hydrosulphites. They contain the necessary catalysts.

Thus—

White Discharge H.A.

250 grms. Hyraldite A. special.
750 ,, starch-tragacanth paste.

Dissolve at 60° C. and cool.

1000

The coloured discharges may be prepared as under:—

	Navy I.N.	Yellow I.N.	Blue I.N.	Green I.N.
Auramine conc.	..	20	..	22·5
Thionine blue G.O.	..	..	20	7·5
Fast marine blue S. extra	30	..	..	..
Water	40	40	120	80
Glycerin	40	40	50	50
Acetin	20	20	20	20
Starch-tragacanth paste	350	360	300	320
Alcohol	30	30	..	..
Tannin 50 per cent. solution in water	100	100	90	100
Turkey-red oil 25 per cent.	40	40	50	50
Discharge paste I.N. 50 per cent. or Discharge paste S. 50 per cent.	350	350	350	350
	1000	1000	1000	1000

Discharge Paste I.N. 50 per cent.

500 grms. hydrosulphite-formaldehyde.
450 ,, starch-tragacanth paste.
50 ,, 2 per cent. solution of Induline scarlet.

1000

Dissolve at 60° C. and warm until the scarlet is reduced.

DISCHARGE PASTE S. 50 per cent.

500 grms. Hyraldite A. special.
500 ,, starch-tragacanth paste or British gum-starch paste.

1000

The addition of aniline or phenol to the above colours in the proportion of 40–50 grms. per kilo. is beneficial, inasmuch as it prevents the premature precipitation of the colour lake. In such cases the alcohol and a portion of the glycerine may be omitted with advantage.

If anything, phenol is preferable to aniline in all hydrosulphite discharges on the Azoic colours developed on the fibre. The aniline colours will keep good for months, especially if formaldehyde be also added, but they yield slightly duller shades than those prepared with phenol.

Another method consists in adding a solution of tannin in glycerine to the discharge pastes containing 2–3 per cent. of phenol. The method resembles the preceding, but is said to yield superior results, the colours being very clear and brilliant. One example will suffice to illustrate the practical application of this process:—

DISCHARGE BLUE T.G.

20 grms. Thionine blue G.O.
30 ,, glycerine.
10 ,, acetine.
140 ,, water.

Dissolve, and add hot to—

200 grms. starch-tragacanth paste.

Heat until the blue is dissolved completely, then cool, and add, when lukewarm—

30 grms. phenol.
90 ,, water. And when cold—
80 ,, tannin-glycerine.
400 ,, 50 per cent. discharge paste I.N.

1000

Other colours are made similarly by replacing the blue with suitable dyestuffs, thus:—

For YELLOW:—20 grms. of either Auramine conc. or Thioflavine T.
For GREEN:— 3 parts yellow.
1 part blue.
For PINK:— 50 grms. Erythrosine A.
100 ,, acetate of chrome 30° Tw. per 1000 grms.

In the pink omit both the tannin-glycerine and the phenol.

TANNIN-GLYCERINE.

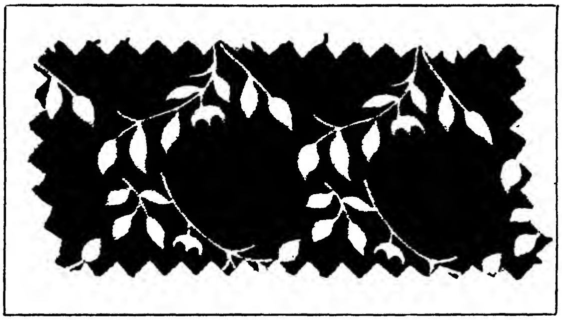
100 parts tannic acid.
60 ,, glycerine.

Heat together until a perfectly smooth syrup is obtained.

Print, steam, fix, and wash all the foregoing colours in exactly the same manner as for Paranitraniline reds.

(*b*) DISCHARGES WITH ANTHRAQUINONE IN THE PRINTING COLOURS.

The only essential difference between the formulæ of these colours and those containing Induline scarlet is in the replacement of the scarlet by a larger quantity of Anthraquinone. In all other particulars, the recipes given above will be a sufficient guide to the preparation of Anthraquinone discharges. The simplest method of effecting the necessary modifications is to prepare a standard discharge paste, containing the requisite proportion of Anthraquinone in the form of a finely ground paste.



α-Naphthylamine Claret discharged with Formosul and Anthraquinone (Clayton Aniline Co., Ltd.).

DISCHARGE WHITE N.F.A.

250 grms. Formosul.
700 ,, starch-tragacanth thickening.
Dissolve at 60° C., cool, and add—
7·5 grms. Anthraquinone ground up in—
42·5 ,, water.

1000

A little glycerine and ammonium oxalate may be added with advantage.

For coloured discharges the proportions given below have yielded good results in practice; other colours may be made on the type of the blue.

DISCHARGE BLUE A.N. ON CLARET.

20 grms. Thionine blue G.O.
30 ,, glycerine.
10 ,, acetine.
100 ,, water. Dissolve, and add to—
200 ,, thick starch-tragacanth paste. Heat again, cool a little, and add—
30 ,, phenol in—
80 ,, water. Cool, and add—
80 ,, tannin-glycerine (see above).
200 ,, sulphoxylate-formaldehyde.
200 ,, starch-tragacanth paste.
6 ,, Anthraquinone.
44 ,, water.

1000

Yellows:—Auramine or Thioflavine.
Greens:— ,, ,, and blue.
Print, steam, and treat generally as for other discharges on clarets, etc.

(c) Discharges with Patent Blue in Printing Colour.

A white discharge on Naphthylamine claret with Patent blue may be made according to the following directions:—

White Discharge P.B.

20	grms.	Patent blue.
80	,,	glycerine.
50	,,	water.
285	,,	starch-tragacanth paste. Boil, cool, and add—
40	,,	phenol.
25	,,	formaldehyde 40 per cent.
250	,,	sulphoxylate-formaldehyde, dissolved in—
250	,,	British gum paste.
1000		

This discharge is only suitable for white patterns, since, in order to obtain pure whites, it must be soaped strongly immediately after steaming, to prevent the leuco compound of the blue from re-oxidising on the fibre.

Any of the Mordant, Sulphur, and Vat colours that are suitable for discharging Paranitraniline red are equally suitable for discharging Naphthylamine claret when combined with Induline scarlet or Anthraquinone.

When *any* hydrosulphite discharge white is to be covered with Aniline black, an addition of both zinc oxide and acetate of soda is essential to the production of a clear-cut white pattern. The best results, too, are obtained when the two colours are printed and steamed separately ; if printed and steamed together, the chlorate of the black is apt to counteract the reducing influence of the hydrosulphite, and thus prevent the perfect discharge of Azoic colour ground. Suitable discharges for this cover style are the following:—

	I.	II.
	grms.	grms.
Zinc oxide	100	100
British gum (light)	100	100
Water	400	370
Boil, cool to 60° C., and add—		
Hydrosulphite-formaldehyde	250	250
1 per cent. sol. Induline scarlet	..	30
Acetate of soda	150	150
	1000	1000

I. is used for Paranitraniline red and Nitrotoluidine oranges.
II. ,, Naphthylamine clarets.

Print the white on the dyed cloth ; steam for 2–3 minutes at 102° C., and then print a prussiate Aniline black cover ; steam again to develop the black, and then wash off and soap as usual.

Satisfactory white and coloured discharges can be obtained on Benzidine and Tolidine chocolates, and on Chloranisidine scarlets, by any of the methods employed for Naphthylamine clarets.

Discharges on Naphthol A.S. Combinations.

In consequence of the increased demand for fast colours, the printing of discharges on grounds of Naphthol A.S. Combinations has, of late, assumed a position of great prominence.

By the use of Naphthol A.S. and its homologues, in place of β-naphthol, it is possible to give a vast variety of fast, multicoloured, and very bright effects on a complete range of ground shades of great beauty and richness.

Dyeing of the Ground Colours.—The concentrations of the naphthol preparing liquors that are necessary to yield given shades are readily ascertained by preliminary trials. As a rule 10–15 grms. per litre are sufficient for full shades, though some strong reds and oranges require as much as 20 grms. per litre and, conversely, some shades of blue, garnet, and violet require as little as 6–8 grms. per litre.

The concentrations of the various diazo-solutions of the colour bases, used for developing, depend entirely on the quantity of naphthol used in preparing the cloth. The relative concentrations of base and naphthol may be found by reference to the tables given on page 544.

The actual preparation of the cloth and its subsequent development are carried out on padding machines according to the method described for the dyeing of plain shades with β-naphthol colours.

It is essential to the success of the dyeing that the goods impregnated with a Naphthol A.S. solution be dried quickly and uniformly on both sides. These conditions are best obtained in a modern hot flue in which the temperature and circulation of hot air are adjustable according to requirements and the passage of the cloth through the chamber is capable of being maintained at a fairly constant speed. Slow drying, faulty circulation of the air current and considerable variations in temperature all tend to promote hydrolysis of the naphthol solution and, consequently, to result in irregular dyeings.

After development in diazo solutions the goods are given an air passage in order to allow complete coupling to take place. The duration of this air passage depends upon the class of cloth in hand and the coupling speed of the developer; but the relatively long air passage for a slow developer or heavy cloth is not detrimental to a quick developer, although it is unnecessary. The fully developed pieces are well washed in cold water and then soaped at the boil in a soap solution containing 3–5 grms. soap per litre, thoroughly washed, and dried ready for printing.

Dyeings of Naphthol A.S.-B.G./Fast scarlet salt G.G.S., of Naphthol A.S./Fast violet B. base, pink combinations of Naphthol A.S.-R.L./Fast red R.L. base, and a few less important dyeings, require a prolonged treatment in boiling soap to bring about the development of their correct shades—a treatment which also enhances their fastness to light, chlorine, and rubbing.

The general process after printing the discharge colours is to steam the goods for about 5 minutes at 215° F. in a rapid ager, with a copious supply of moist, air-free steam, then for single white discharges to soap the pieces at the boil for about 5 minutes in slightly alkaline soap, followed by a thorough wash in hot and cold water. Coloured discharges are treated, before soaping, in perborate of soda or tartar-emetic, according to the type of dyestuff employed for discharging.

Discharging the Dyed Ground Colours.—At the present time the only discharging agents employed for this purpose are the stable sulphoxylate-formaldehyde compounds such as Rongalite, Formosul, or Britulite, and all practical processes are based on their use.

For white discharges, Rongalite C., etc., *alone* may be used in some cases, but, for the most part, better results are obtained from mixtures of Rongalite C., potassium carbonate and anthraquinone, to which additions of zinc oxide and Dissolving Salt B. are frequently made for the purpose of increasing the activity and effect of the discharging agent. For coloured discharges several groups of dyestuffs are available, viz., Basic, Chrome mordant, Sulphur, Pigment, and Vat colours, all of which are in regular use for different styles and qualities of work. In view of the fastness of the ground colours, however, it is preferable to employ vat dyestuffs, since they are not only easy to apply but also provide an extremely wide range of bright and exceedingly fast discharge colours; vat colour discharge patterns on grounds of Naphthol A.S. dyeings yield prints of the highest tinctorial quality and represent the acme of fastness obtainable in discharge work.

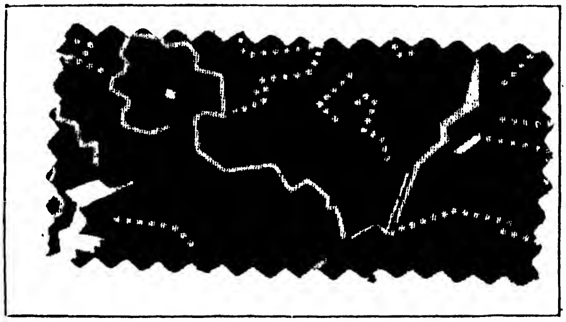
As all Naphthol A.S. dyeings, with the exception of those on Naphthols A.S.-G. and A.S.-B.R., are readily dischargeable by reduction methods based on sulphoxylate-formaldehyde compounds, and as practically all vat colours of the Indanthrene, Caledon, and Cibanone series (and selected members of other groups) are suitable for coloured discharges, it is obvious that an enormous number of permutations of colour is obtainable by this method of working. Some idea of the scope and practical value of the method may be gathered from the fact that its wide range of colour possibilities, each easily realisable by *one speedy process common to all*, embraces many combinations which reproduce, in an improved form, certain classic styles and colour effects that, formerly, demanded *separate and distinct processes* for their execution—processes which involved the carrying-out of many long and tedious operations such, for example, as Turkey red dyeing, Indigo dyeing, the dyeing of Alizarine and vegetable colouring matters on various mordants, of Basic colours on tannin mordants, of Mordant colours on chrome mordants, and numerous combinations of these and other distinct styles. By the discharge process on Azoic colour grounds all these lengthy and diverse individual treatments are replaced by a single comprehensive method of working which is capable of being applied to nearly all the purposes for which bulky installations of costly special plant were previously indispensable.

The style, however, has its limitations. Brilliant blue and green grounds, and many of the quieter mode shades, are still outside the range of Azoic colours and must still be dyed by other methods. None of the Azoic blacks, either, finds any employment as dischargeable ground colour, nor are they necessary, Aniline black being more convenient and of excellent fastness. But for medium and dark shades of all types of oranges, reds, clarets, browns, blues, and a rather quiet green, the Azoic colours of the Naphthol A.S. type are unsurpassed as ground shades of great beauty and fastness and, when discharged with vat dyestuffs, they give prints of the highest quality.

Suitable combinations of A.S. Naphthols and Fast Bases are detailed in an earlier section of this work under "Naphthol A.S." They may be used as there given, or modified in strength according to the depth of shade desired. Other particulars concerning relative proportions will be found in the tabular survey in the same section. As the printing colours are applicable to all dischargeable grounds, the following examples will illustrate sufficiently the general method of working.

VAT COLOUR DISCHARGES.—Indanthrene colours and colours of their type, and certain Algole and Indigoid dyestuffs of the Ciba and Durindone groups, are generally preferred for discharge work on account of their fastness. The printing colours are made up in the same manner as for white grounds and, if necessary, Anthraquinone is added and the quantity of Rongalite increased.

The pattern illustrated is typical of a Turkey-red style, executed in Vat and Azoic colours.



Naphthol A.S.-D./Fast Red K.B. base, discharged with Vat Colours (I.G.).

NAPHTHOL PREPARE.

18 grms. Naphthol A.S.-D.
20 c.c. Monopol Brilliant Oil.
22·5 ,, caustic soda 62° Tw.
2 grms. Nekal B.X.

To 1000 c.c.

DEVELOPING BATH: FAST RED K.B.

16·2 grms. Fast red K.B. base.
200 c.c. water.
16·2 ,, hydrochloric acid 32° Tw.

Add—

6·5 grms. sodium nitrite.
30 c.c. water.

Allow to stand ½ hour, then add—

13 grms. sodium acetate.
60 c.c. water.

Make up to 1 litre

PRINTING COLOURS.

White Discharge 150.

500 grms. neutral starch-tragacanth paste.
150 ,, Rongalite C. (or Formosul).
200 ,, zinc oxide 50 per cent. paste.
50 ,, Solution Salt B.
30 ,, carbonate of potash.
40 ,, Anthraquinone 30 per cent. paste.
30 ,, water.

1000

Yellow Discharge.

100	grms.	Indanthrene printing yellow G.O.K. double paste fine.
80	,,	glycerine.
30	,,	Solution Salt B.
200	,,	neutral starch-tragacanth paste.
300	,,	British gum thickening 1 : 1.
100	,,	carbonate of potash.
125	,,	Rongalite C.
65	,,	water.
1000		

Green Discharge.

As yellow, but with 150 grms. Indanthrene brilliant green 4 G. double paste fine per 1000 grms. colour.

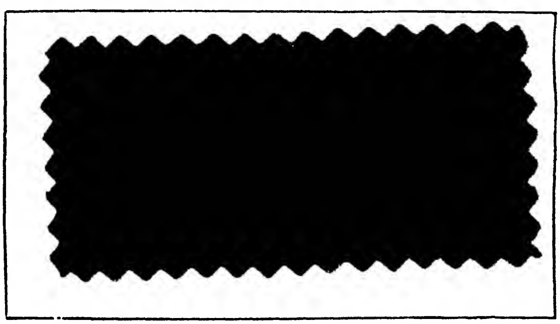
Blue Discharge.

150	grms.	Indigo M.L.B./4 B. (or Ciba blue 2 B.) 20 per cent.
80	,,	glycerine.
30	,,	Solution Salt B.
200	,,	neutral starch-tragacanth paste.
300	,,	British gum thickening 1 : 1.
80	,,	carbonate of potash.
25	,,	Rongalite C.
135	,,	water.
1000		

Black (Direct Print).

200	grms.	Indanthrene printing black B. paste.
410	,,	neutral starch-tragacanth paste.
135	,,	water.
160	,,	carbonate of potash.
35	,,	Rongalite C.
35	,,	water.
25	,,	Depanol J. (a special solvent).
1000		

The cloth, prepared with Naphthol A.S.-D. and dried in the hot flue, is developed, in a mangle, with Fast red K.B., washed, soaped at the boil, and dried. It is then printed with the foregoing discharge colours and, after steaming for 5 minutes in the rapid ager, is passed in succession through a bath of perborate of soda and acetic acid (to re-oxidise the vat colours), a series of washing becks, a bath of boiling soap, and finally a cold water washing machine.



Naphthol A.S.-D./Fast Red salt R.L., discharged with Vat Colours (I.G.).

The attached pattern illustrates the production of discharges on an extremely fast claret ground.

PREPARE.

15 grms. Naphthol A.S.-D.
20 c.c. Monopol Brilliant Oil.
22·5 ,, caustic soda 62° Tw.
2 grms. Nekal B.X. (optional, but advantageous).

To 1000 c.c.

DEVELOPING BATH.

52·5 grms. Fast red salt R.L.
300 c.c. water at 75°–85° F.

Dissolve and make up with cold water to—

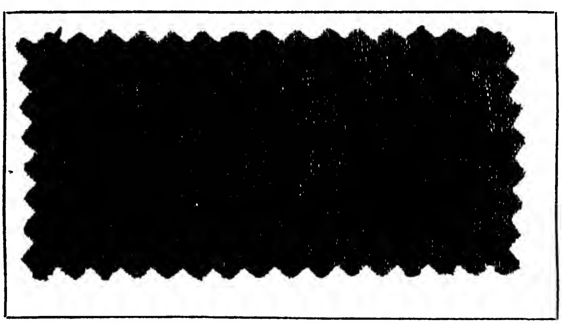
1000 c.c.

DISCHARGE COLOURS.

	Light Blue.	Light Brown.
Indanthrene brilliant blue 3 G. paste fine	100 grms.	..
Algole brown 3 R. paste fine	..	200 grms.
Glyecine A.	50 ,,	..
Glycerine	..	80 ,,
Neutral starch-tragacanth paste.	200 ,,	200 ,,
Carbonate of potash	100 ,,	90 ,,
Rongalite C.	125 ,,	120 ,,
British gum thickening 1 : 1	300 ,,	280 ,,
Water	125 ,,	..
Solution Salt B.	..	30 ,,
	1000	1000

The prepared and developed cloth is printed with the discharges and after-treated in exactly the same manner as the preceding pattern—Fast red K.B.

The same Naphthol A.S.-D. prepare developed in Fast orange G.C. base gives the fine orange ground shown in the following pattern, which also illustrates the printing of Rapid Fast colours along with discharge colours.



Naphthol A.S.-D./Fast Orange G.C. base, discharged with Vat Colours (I.G.).

PREPARE.

15 grms. Naphthol A.S.-D. per litre.

DEVELOPING BATH.

11·25	grms.	Fast orange G.C. base.
150	c.c.	hot water.
13·5	,,	hydrochloric acid 32° Tw.

Mix and dissolve by adding—

300	c.c.	cold water.

Cool to 40° F. with ice, if necessary, then add—

5·2	grms.	sodium nitrite in
40	c.c.	water.

Allow to react for 15 minutes and then neutralise with—

11	grms.	sodium acetate in
40	c.c.	water.

Make up to 1 litre

DISCHARGE COLOURS.

	Light Blue.	Dark Blue.
Indanthrene blue G.C.D. double paste fine	50 grms.	..
Indanthrene printing blue R. paste	..	150 grms.
Indanthrene navy blue R.R.D. paste fine	..	50 ,,
Glycerine	80 ,,	80 ,,
Solution Salt B.	..	30 ,,
Neutral starch-tragacanth paste	200 ,,	165 ,,
British gum thickening 1 : 1	300 ,,	300 ,,
Carbonate of potash	60 ,,	100 ,,
Rongalite C.	60 ,,	125 ,,
Water	250 ,,	..
	1000	1000

RED (Direct Print).

120	grms.	Rapid Fast red G.L. paste.
20	,,	Monopol Brilliant Oil.
50	,,	neutral chromate solution.
310	,,	water.
500	,,	neutral starch-tragacanth paste.
1000		

The prepared and developed goods are printed, steamed, etc., exactly as for Fast red K.B. base dyeings. The development of the Rapid Fast red G.L., partly effected during steaming, is completed in the acidified perborate bath used for re-oxidising the vat colour discharges.

Yellower orange grounds may be obtained with the same base on Naphthol A.S.-O.L., and redder oranges from the combination Naphthol A.S./Fast orange G.R. base.

Dark blue fabrics, whether plain or printed, have always figured amongst the most important articles of commerce in all markets of the world. For a long time Indigo was pre-eminent, but with the introduction of faster vat dyestuffs in the first place and, later, of dark blue Azoic colours of excellent fastness, its position was gradually undermined, and to-day, though still of importance for many purposes, it ranks only as *a* fast blue, not *the* fast blue.

For the production of fast discharge styles on Navy blue grounds the Azoic blues are much more convenient than Indigo ; they are easily and rapidly dyed, and are as easily discharged, the process conforming to that in use for all other dischargeable Naphthol A.S. colour grounds.

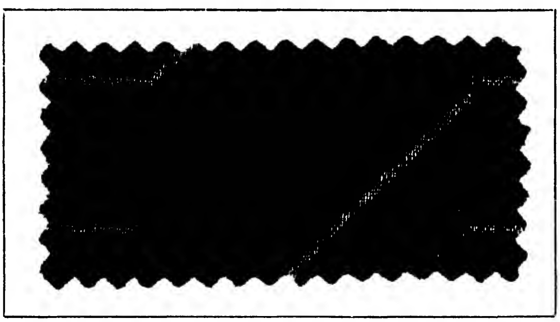
For standard shades of Navy blue the combination of Naphthol A.S. with Variamine blue B. is the most popular, as it is readily dischargeable and possesses excellent fastness and brightness. Redder and deeper shades are produced with Naphthol A.S.-D., A.S.-R.L., or A.S.-O.L. The brightest blue is yielded by Naphthol A.S., but if blues of light or medium shades are required, Naphthol A.S.-E. is preferable on account of its better reducing property.

For blues of greater brilliancy than Variamine blue B. two additional bases are available, viz. Fast blue R.R. base and Fast blue B.B. base and their corresponding Fast Colour Salts. The former gives purplish blues and the latter somewhat greener and, in light shades, much brighter blues than Variamine blue B. Both are faster to chlorine than Variamine blue, but are slightly inferior in fastness to light.

Cheap blues of good fastness to washing, but poor to light, may be dyed with Fast blue B. base on Naphthol A.S., A.S.-D., or A.S.-O.L. They are useful for goods which are not required to stand exposure to light and, as they possess extremely strong tinctorial power, they are very cheap to dye.

Of these various blues, Variamine blue B. in the form of its base, or Fast Colour salt, is the most generally useful on account of its close approach in shade to Indigo and because it is applicable to a wider range of effects than other blues.

Apart from slight differences in the preparation of the diazo developing solution, Variamine blue styles are worked in practically the same manner as are other Naphthol A.S. discharges.



Naphthol A.S./Variamine Blue B., discharged with Vat Colours.

PREPARE.

15 grms. Naphthol A.S.
20 c.c. Monopol Brilliant Oil.
22 c.c. caustic soda 62° Tw.

To 1000 c.c.

DEVELOPING BATH.

710 c.c. Diazo solution V.B.
290 c.c. water.

1000

SODA BATH.

10–12 grms. soda-ash per litre.

DIAZO SOLUTION V.B.

(1)
24 grms. Variamine blue B. base.
200 c.c. hot water at 200° F.
35 ,, hydrochloric acid 32° Tw.

Dissolve and pour hot into—

(2)
500 c.c. water at about 60° F.
6·5 grms. sodium nitrite.

Stir well and allow to stand for about 10 minutes ; then add—

40 grms. sodium acetate.

Make up to 1000 c.c.

When (1) and (2) are added together the temperature of the mixture ought to mark 95°–110° F. At low temperatures the diazotisation is incomplete, and a portion of the base comes out of solution as a rule. Diazotisation may be carried out at as high a temperature as 140° F. without detriment.

The goods, padded in the naphthol solution and dried in hot flue as usual, are developed in a mangle, given an air passage of at least ½–1 minute, and then passed *at once* through the soda bath at 65°–85° F., washed, soaped at the boil, washed, and dried. The soda treatment is performed in a roller beck of about 1200 litres capacity, and is essential to the full development of the shade, which is not completely effected during the passage through the diazo solution in the padding mangle.

Instead of the diazo solution of Variamine blue B. base it is frequently more convenient to use the stable diazo compound, Variamine Blue Salt B. Thus:

Developing Bath.

34 grms.	Variamine Blue Salt B.
17 ,,	acetic acid 50 per cent.
250 c.c.	hot water.

Dissolve and make up to 1000 c.c.

The result is the same and the process remains otherwise unaltered.

An interesting and important innovation in the dyeing of Variamine blue has recently been recommended. It has been found that if the developed goods are passed directly from the developing machine through a small high-temperature steaming box and steamed for ¼–½ minute at 230°–240° F., the dyeings come out about two-thirds stronger, coupling is perfectly effected, and the dyed ground discharges to a better white than when dyed by the usual methods. A suitable steaming box for this process is shown in fig. 78.

By whatever method developed, the goods are afterwards washed well, soaped at the boil, washed again, dried, and printed with the following colours as shown in the pattern:—

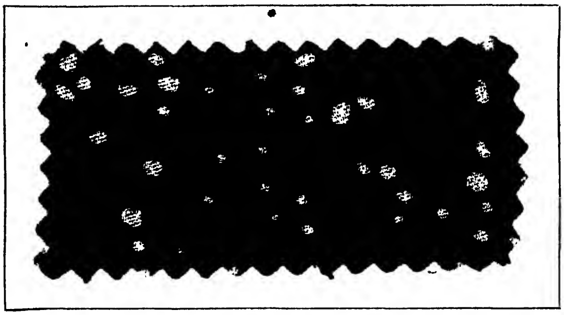
Discharge Colours.	Yellow. grms.	Green. grms.	Blue. grms.	Red. grms.
Indanthrene printing yellow G.O.K. double paste	100	..	..	..
,, brilliant green 4 G. double paste fine	..	150	..	..
,, brilliant blue 3 G. paste fine	..	..	100	..
,, brilliant pink R. paste	..	..	..	250
,, brilliant orange R.K. paste	..	..	..	50
Glycerine	80	80	..	80
Glyecine A.	..	..	50	..
Solution Salt B.	30	30	..	30
Neutral starch-tragacanth paste	200	200	200	165
British gum thickening 1 : 1	300	300	300	200
Carbonate of potash	100	100	100	75
Rongalite C.	125	125	125	150
Water	65	15	125	..
	1000	1000	1000	1000

White Discharge.

The same as for Fast red K.B., p. 646.

After printing, the goods are steamed for 5 minutes, passed through a bath of perborate and acetic acid, washed, soaped at the boil, washed, and dried.

The same colours and process are applicable to dyeings of Fast blue B.B. and R.R. bases and Fast blue B. base on various naphthols, but the bases must be diazotised in the cold as usual.



Naphthol A.S./Fast Violet B. base, discharged with Vat colours (I.G.).

A fine and easily dischargeable bright violet ground is produced by Fast violet B. base, or Fast violet salt B., on a Naphthol A.S. prepare. In shade it approaches closely to that of Methyl violet dyed on tannate of antimony mordant but, being of good all-round fastness, it yields, when discharged with vat colours, a much superior article to that given by the so-called "Vat-tannic style."

Prepare.

7·5	grms.	Naphthol A.S.
20	c.c.	Monopol Brilliant Oil.
11·5	,,	caustic soda 62° Tw.

To 1000 c.c.

Developing Bath.

8·5	grms.	Fast violet B. base.
2·5	,,	sodium nitrite.
30	c.c.	hot water.

Make into a smooth paste, cool down, and stir into—

9·5	c.c.	hydrochloric acid 32° Tw.
250	,,	cold water.

Allow to react for ½ hour, then neutralise with—

3·3	grms.	sodium bicarbonate.
50	c.c.	cold water.

Finally adding—

8·7	grms.	Epsom salts ($MgSO_4$).
50	c.c.	water.

To 1000 c.c.

The goods, prepared, developed, and soaped in the usual manner, are printed with the same discharge colours as those described for other examples of the style and then steamed, etc., according to the general process.

In place of Fast violet B. base the corresponding quantity of Fast violet salt B. may be used, with equally good results, for developing; it is simply dissolved in warm water and cooled before use.

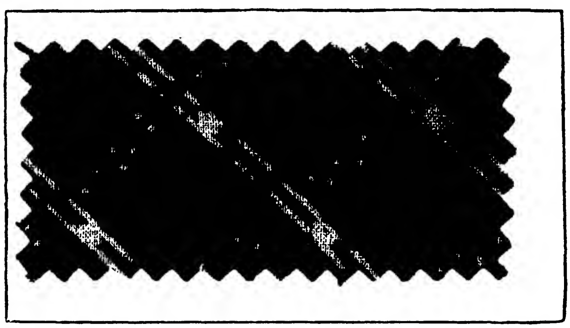
1 part Fast Violet B. base = 5 parts Fast Violet salt B.

The salt, and indeed all the Fast Colour salts, is more expensive than the base, but is more convenient on the small scale, and saves a good deal of time.

Naphthol A.S.-G.R. (Brenthol N.G.) is the only naphthol, to date, which yields a green with any amino-base. With Fast blue B.B. base or Variamine blue B. base, or their stable diazo salts, it gives pleasing full-green shades which fill a gap in the Naphthol A.S. range.

Owing to its great affinity for the cotton fibre, Naphthol A.S.-G.R. is unfitted for the direct printing of bases on naphtholated cloth; it cannot be washed out and it is, consequently, impossible to obtain a clear white ground. On the other hand, it lends itself admirably to the production of discharge styles on all types of cotton and rayon fabrics. The dark bluish-greens obtained with the blue bases mentioned above are of excellent fastness to washing, good fastness to chlorine, and moderately good fastness to light, and they are easily dischargeable to a clear white with Rongalite C., and in colours, with vat dyestuffs.

The strong substantivity of Naphthol A.S.-G.R., which excels that of any other naphthol, endows it with the properties of a direct dyestuff and causes it to fix itself on the fibre at an excessively rapid rate during the padding process. In other words, the cloth under treatment with a solution of Naphthol A.S.-G.R. acts as a solid solvent, and extracts more naphthol from the padding liquor than is represented by the volume of padding liquor absorbed. As a result, the naphtholate padding liquor becomes exhausted unless means are adopted to maintain its original concentration. In practice, this substantivity (or affinity for the cotton fibre) of Naphthol A.S.-G.R. is allowed for, when working on a three-bowl double immersion padding mangle, by *reducing the strength of standard naphtholate solution* to 1 : 1 or 1 : 2 for a 40 litre box, afterwards feeding-in full strength standard solution to keep the liquor in the padding box at a constant level. It is also important to carry-out the padding at as near the boil as possible—about 190°–195° F.—as the substantivity diminishes as the temperature rises.



Naphthol A.S.-G.R./Fast Blue B.B. base, discharged with Vat colours (I.G.).

The pattern illustrated has been produced according to the following formulæ:—

STANDARD PREPARE G.R.

18 grms. Naphthol A.S.-G.R.
20 c.c. methylated spirit.
20 „ water.
5 „ caustic soda 70° Tw.

Stir for about 5 minutes until complete solution is obtained and then stir slowly into—

800 c.c. water at 195° F.
10 „ caustic soda 70° Tw.
10 „ Monopol Brilliant Oil.

To 1000 c.c.

At the outset the liquor box (40 litres) of the preparing mangle or padding machine is filled with one or other of the following dilute prepares, according to the speed of the machine:—

(A.)	(B.)		
13—	20	litres	standard prepare G.R.
26—	20	,,	boiling water.

Working temperature 190°–195° F.

(A.) is for a slow-running machine, (B.) for a quicker machine. The correct relationship between speed of preparing and initial dilution of the preparing liquor is a question of experiment on the particular plant in use. As the goods take up the preparing solution in the course of running, the padding-box must be replenished with *full strength standard prepare* at a rate regulated to maintain a constant level; the level of the liquor must not be allowed to drop to any appreciable extent, otherwise the prepare will become progressively weaker, owing to absorption of naphthol in greater proportion than water, and uneven dyeings will result.

After preparing and drying, the goods are developed in—

DEVELOPING BATH.

11 grms. Fast blue B.B. base.
300 c.c. cold water.

Make into a smooth paste and dissolve with—

11 c.c. hydrochloric acid 32° Tw.

Add slowly with stirring—

3 grms. sodium nitrite.
50 c.c. cold water.

Allow to react for 15 minutes, and then neutralise with—

5 grms. sodium acetate.
50 c.c. water.
10 c.c. acetic acid 50 per cent.

Make up to 1000 c.c.

then being given 1 minute's air passage, washed, soaped at the boil, washed, dried, and printed as follows:—

COLOUR DISCHARGES.

	Yellow.	Orange.
Indanthrene yellow 3 G. "Suprafix" double	150 grms.	..
Indanthrene brilliant orange G.R. "Suprafix"	..	150 grms.
Glycerine	50 ,,	50 ,,
Water	200 ,,	200 ,,
Starch-tragacanth paste	400 ,,	400 ,,
Carbonate of potash	90 ,,	90 ,,
Rongalite C.	100 ,,	100 ,,
Anthraquinone 30 per cent. paste	10 ,,	10 ,,
	1000	1000

2½ per cent. Dissolving Salt B. may be added with advantage.

WHITE DISCHARGE.

350	grms.	starch-tragacanth paste.
250	,,	Rongalite C.
100	,,	water.
50	,,	Dissolving Salt B. 1 : 1.
50	,,	Leucotrope W. conc.
60	,,	caustic soda 70° Tw.
100	,,	zinc oxide 50 per cent. paste.
40	,,	Anthraquinone 30 per cent. paste.
1000		

Reduce 2 : 1 for use with the green ground described above.

After printing, the pieces are steamed for 3–5 minutes in the rapid ager with air-free steam at 214°–216° F., thoroughly washed in cold water, treated in dilute caustic soda (5 c.c. NaOH 70° Tw. per litre) at 195°–200° F., washed, soaped at the boil, washed, and dried. A passage through a perborate of soda bath before treating in hot dilute caustic soda promotes the re-oxidation of the vat discharges and is a preventive against their partial solution in the alkali.

BASIC COLOUR DISCHARGES.—The Basic colours are of less importance than Vat colours for discharging purposes, as the printed discharges, fixed in the rapid ager only, are much inferior in fastness to the dyed ground shades. This disadvantage is most apparent when white discharges are to be printed in combination with colours, as the presence of the latter precludes a treatment in boiling soap, which is almost essential to the production of a good and permanent white on all Azoic colour grounds.

Nevertheless, the Basic colours are employed for many of the more ordinary qualities of work and, if restricted to the most easily dischargeable grounds, it is quite possible to obtain satisfactory white discharges in multicolour patterns. Suitable grounds for the purpose are combinations of :—

GROUND COLOURS.

Oranges :—	Naphthol A.S.-D.	Fast Orange G.C. base.
	,, A.S.-D.	,, ,, G.R. base.
Red, Scarlet, and Pink :—	Naphthol A.S.	Fast Red K.B. base.
	,, A.S.-D.	,, Scarlet R.C. base.
	,, A.S.-B.S.	
Bordeaux and Claret :—	Naphthol A.S.-D.	Fast Red T.R. base.
	,, ,,	,, ,, R.L. ,,
	,, A.S.-R.L.	,, ,, B. ,,
	,, ,,	,, ,, R.L. ,,
	,, A.S.-B.O.	,, ,, B. ,,
	,, A.S.	Fast Bordeaux G. P. base.
Blue :—	Naphthol A.S.	Fast Blue B. base.
Chocolate :—	Naphthol A.S.-D.	Mixture of Fast Black salt K. and Fast Scarlet salt G.G.S.

Any Basic dyestuff, of whatever make and group, that is not destroyed by

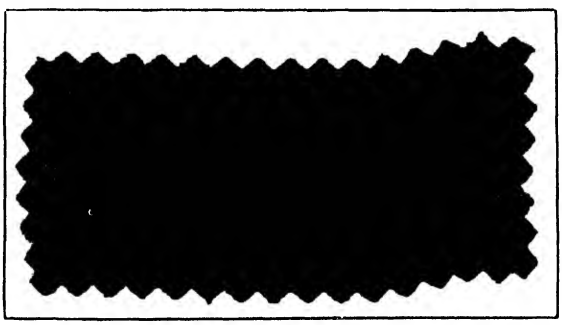
Rongalite C. may be used for coloured discharges. Amongst these may be mentioned :—

Citroflavine 8 G. 45.	Tannoflavine T.	Thioflavine T.
Acridine Orange N.O.	Rhoduline Orange N.O.	Euchrysine R.R.D.X.
Flavophosphine, all brands.	Coriphosphine O.X.	Sabaphosphine O.
Rhodamine 6 G.H. extra.	Rhodamine B.	Irisamine G.
Acronol Blue G.O.	Thionine Blue G.O.	Methylene Blue 3 G.X.
Discharge Navy Blue N. extra conc., etc.		New Fast Grey.

Greens are produced from mixtures of various blues and yellows, violets from Rhodamine B. and blues.

Either tannic acid or Katanol O.N. is used as mordant for Basic colour discharges. Tannic acid is invariably mixed with the printing colours, in the usual way, whereas Katanol O.N. is applied as a separate mordant to the pieces before printing. The latter entails an extra process, but it also imparts better fastness to washing and permits of the discharge colours penetrating much more deeply into the fibre—an advantage of some importance in the printing of flannelettes and other raised goods. The colours employed for the Katanol method of fixation contain no precipitable matter, are more soluble, and so are more readily absorbed by the fabric.

The pattern illustrated has been printed with Basic colours and tannin.



Naphthol A.S./Fast Blue salt B.. discharged with Basic colours (I.G.).

PREPARE.

6	grms.	Naphthol A.S.
20	c.c.	Monopol Brilliant Oil.
10	,,	caustic soda 62° Tw.

To 1000 c.c. with water.

DEVELOPING SOLUTION.

18	grms.	Fast blue salt B.
300	c.c.	water at 75°–85° F.
18	grms.	sodium bicarbonate.

To 1000 c.c. with water.

Prepare, dry, and develop, soap at the boil, etc., in the usual manner, then print with the following :—

Discharge Colours.

	Yellow.	Green.
Citroflavine 8 G. 45	57 grms.	30 grms.
Rhoduline orange N.O.	3 ,,	..
Thionine blue G.O.	..	20 ,,
Glyecine A.	80 ,,	80 ,,
Water	100 ,,	110 ,,
Starch-tragacanth paste	400 ,,	400 ,,
Rongalite C. (finely ground)	150 ,,	150 ,,
Tannic acid	75 ,,	75 ,,
Methylated spirit	75 ,,	75 ,,
Gum arabic solution 1 : 1	60 ,,	60 ,,
	1000	1000

After printing, the goods are steamed for 5 minutes in the rapid ager at 215° F., then fixed at full width by a passage through a bath of tartar-emetic and chalk at 120° F., washed, open soaped at 120° F., washed, and dried.

Glyecine A. in the above recipes may be replaced by 30 grms. glycerine and 90 c.c. methylated spirit, plus an addition of 30 grms. aniline or phenol to inhibit precipitation of the dyestuff.

Working by the Katanol process the dyed pieces are padded in a solution of

15–20 grms. Katanol O.N.,
$1\frac{1}{2}$–2 ,, soda-ash,
1000 c.c. water,

at 120° F., dried and printed with discharge colours made-up on the lines of the following formula :—

Typical Recipe.

50	grms.	Basic dyestuff.
70	c.c.	methylated spirit.
30	,,	Acetine N.
250	,,	water.
400	,,	British gum thickening 1 : 1.
200	,,	Discharge thickening (below).
1000	c.c.	

Discharge Thickening.

120	grms.	Rongalite C. (or more if required).
140	,,	gum tragacanth mucilage 65 : 1000.
40	,,	water.
300		

For better penetration of thick, raised materials it is advisable to use tragacanth thickening alone.

Print, dry, steam for 5 minutes, pass at full width through a bath at 85°–105° F. containing 2 grms. Katanol O.N. per litre, wash and chrome lightly, wash, soap at 110°–120° F., wash, and dry.

Sulphur and Chrome Colour Discharges.—Neither of these styles is used to any great extent to-day. The Sulphur colours are occasionally useful for goods not required to stand chlorine, but otherwise of excellent general fastness, whilst the Chrome mordant colours are, for the most part, employed only as supplementary colours or for the production of single-colour dark blues on red or claret grounds.

Any Sulphur colour printing paste, suitable for direct printing on white grounds, may be converted into a discharge colour by adding the requisite amount of Rongalite, all subsequent processes being identical with those used for vat colour discharges. Typical recipes will be found on pp. 635 and 636.

The application of Chrome mordant colours to Azoic colour discharge work has been dealt with already on pp. 632 and 633, and what has been described there applies equally here.

Rapidogen Dyestuffs Padded and Discharged.—The Rapidogen dyestuffs, usually regarded solely as printing colours, are also well adapted to the production of pad dyeings on cotton and artificial silk fibres. They afford a quick and very convenient means of obtaining easily dischargeable Azoic colour grounds, and they possess the valuable property of *dyeing both fibres alike in mixed fabrics of cotton and viscose silk or rayon*—a desideratum which presents difficulties when dyeing Azoic colours by the usual processes of preparing in naphthols and developing with diazo solutions.

The manner of dyeing Rapidogens is identical with that for direct printing, except that the goods are slop-padded through a mangle instead of being printed by an engraved roller. The unprepared cloth is padded through one of the following colour solutions, dried, and then developed by an acid treatment in a second padding machine or a rapid ager, according to choice.

Colour Solutions.	*A.* grms.	*B.* grms.	*C.* grms.
Rapidogen dyestuff	60	80	80
Caustic soda 70° Tw.	30	30	30
Monopol Brilliant Oil	30	30	30
Glyecine A.	30	..	..
Water at 105°–120° F.	200	200	200
Tragacanth thickening 60 : 1000	50	50	50
Urea	50	..	..
Neutral chromate solution (*q.v.*)	..	50	..
Cold water	550	560	610
To	1000 grms.		

Solution (*A.*) is for Rapidogen Blue R. and Green B.
,, (*B.*) ,, ,, Rapidogen Bordeaux R.
,, (*C.*) ,, ,, all other Rapidogen dyestuffs, except Rapidogen Blue B., which is dissolved *cold* with methylated spirit in place of Monopol Oil.

After padding, the goods are dried in the hot-flue and then developed by padding in a *cold* mixture of—

25 c.c. acetic acid 50 per cent.,
25 ,, formic acid 90 per cent.,
20 grms. Glauber's salt,
1000 c.c. water,

drying directly on a cylinder drying machine attached to the padding mangle.

The development of the padded colours may also be effected on an open soaper by a short passage through an almost boiling mixture of—

20 c.c. acetic acid 50 per cent.,
5 ,, formic acid 90 per cent.,
25 grms. Glauber's salt,
1000 c.c. water,

at about 205°–212° F. or more simply still by steaming the goods in a rapid ager, or other enclosed chamber, in an atmosphere of steam and acid vapours obtained by allowing a mixture of equal parts of acetic acid 50 per cent., and formic acid 90 per cent., to fall slowly on to a steam-heated chest situated inside the ager close to the inlet for the goods.

After developing by one or other of the foregoing methods (see also " Printing of Rapidogen Dyestuffs") the goods are washed and soaped as usual and then printed with any of the Rongalite discharges used for ordinary Azoic colour grounds.

Destructive Action of Moist Air on Hydrosulphite Discharges.

All hydrosulphite discharges depend, to a very large extent, for their success upon the conditions under which they are carried out. The necessity for the absence of air in the steaming apparatus has already been pointed out, but, in addition to this, it is imperative to avoid exposing the printed goods, either before or after steaming, to the action of warm moist air. This cannot be too much insisted upon. Hydrosulphite-formaldehyde compounds, though stable in a dry atmosphere, are readily oxidised in presence of moisture at even the ordinary temperature, and, consequently, when exposed to moisture, in thin films such as exist on printed goods, they rapidly lose their discharging properties. If, therefore, steaming cannot be proceeded with *immediately* after printing, the goods must be covered up and stored in a warm and perfectly dry atmosphere. Neglect of this precaution leads to imperfect discharges owing to a partial decomposition of the discharging agent.

Again, after steaming, the white discharges are very liable to turn brown or yellow if the goods are allowed to lie exposed for any length of time in a warm humid atmosphere. In this case the defect arises from a quite different cause, viz. the oxidation of the aminonaphthols formed by the scission of the N : N group in the Azoic colour ground when this latter is reduced by hydrosulphites in steaming. With α-Naphthylamine claret, for example, the reaction may be expressed as follows :—

$$\underset{\alpha\text{-Naphthylamine claret.}}{C_{10}H_7N : NC_{10}H_6(OH)_\beta} + 2NaHSO_2 + 2H_2O = \underset{\text{Aminonaphthol.}}{NH_2.C_{10}H_6.OH} + C_{10}H_7NH_2 + 2NaHSO_3$$

The presence of bisulphite of soda retards the oxidation for a short time, but as soon as it becomes converted into the bisulphate (or sulphate) the aminonaphthol begins to turn brown, especially if, as is usually the case, the original discharge was slightly alkaline when printed. Once this brownish stain develops it is impossible to remove it by any known means. Its formation can be prevented by the same means as employed for protecting the goods *before* steaming, *i.e.* by storing in a dry place, or, better still, by washing and soaping them immediately after steaming, when all sensitive decomposition products are removed completely from the fibre, leaving a pure permanent white discharge.

Resists under Hydrosulphite Discharges.

As already noted above, oxidising agents neutralise the discharging properties of the hydrosulphites, and on this fact is founded a useful resist style.

The dyed cloth is first printed with a thickened solution of an oxidising agent, and then over-printed with a hydrosulphite discharge paste. On steaming, the hydrosulphite discharges the colour only from those parts of the cloth upon which no oxidising agent has been printed. The presence of

organic acids improves the resist, and for resists under coloured discharges the addition of tartar-emetic is essential. Chlorate of soda is the oxidising agent most commonly employed, but in certain cases persulphates, chromates, manganese dioxide, and copper salts may be used with advantage. An alkaline copper solution is especially suitable for reserving Para brown and Benzidine chocolate ; it cannot be used for reds and clarets on account of its action on these colours, which it converts into dirty brown shades. Basic colour discharges are resisted with antimony salts ; Modern blue, Blue 1900, and other colours of the Gallocyanine series, with antimony salts and chlorate when they contain tannin, and with chlorate alone when they are fixed with chromium oxide without tannin. Chromoglaucine blue is resisted in the latter way also ; and all the various resists contain a certain amount of citric or tartaric acid.

The following recipes are typical of the methods employed for counteracting the reducing action of hydrosulphite discharges on the insoluble Azoic colours :—

WHITE RESISTS.

	I.	II.	III.	IV.	V.
British gum paste	600	550	525	800	650
Citric acid	50	75	75	100	150
Chlorate of soda	150	150	200	100	200
Sodium tartar emetic	..	225	200	..	..
Oxalate of antimony	200	..	..	..	..
	1000	1000	1000	1000	1000

Nos. I., II., and III. are chiefly used under basic colour discharges, but they are equally efficient under two-colour cover prints in white and basic colours. No. IV. is for resisting a white discharge on Paranitraniline red, Para brown, and other Azoic dyes, while No. V. is employed under mordant colours fixed with chromium acetate alone. Such colours as Modern blue, Blue 1900, etc., which contain tannin as well as chromium acetate, may be satisfactorily resisted by Nos. I., II., or III.

ALKALINE COPPER RESIST.

200 grms. dark British gum.
250 ,, water. Mix to a smooth paste and add slowly—
150 ,, caustic soda 100° Tw. Warm to 60°–70° C., then cool, and add—
400 ,, alkaline copper solution.

1000

Used under white discharges on Para brown and Benzidine and Tolidine chocolates.

ALKALINE SOLUTION OF COPPER.

400 c.c. copper chloride 105° Tw.
120 ,, water.
250 grms. tartaric acid.
200 c.c. glycerine. Dissolve, cool, and in the cold mix with—
480 ,, caustic soda 105° Tw.
100 ,, water.

Make up to 1550 c.c.

Another resist used in practice with excellent results for the " Para brown cover white style " consists in the main of chlorate and chromate of soda, with the addition of aluminium acetate.

RESERVE FOR PARA BROWN.

70	grms.	chlorate of soda.
50	,,	bichromate of soda.
{ 90	,,	water.
{ 75	,,	British gum.
150	,,	acetate of alumina 20° Tw.
20	,,	acetic acid.
50	,,	caustic soda 70° Tw.
15	,,	olive oil.
10	,,	turpentine.
530		Boil and cool.

The caustic soda ought to be added to the solution of bichromate in the gum paste before the aluminium acetate is introduced. Print on the brown-dyed cloth, dry, cover in any suitable hydrosulphite discharge white, steam, etc. as usual. By printing a discharge white along with the reserve, and then throwing a delicate cover pattern in white over the whole, very pretty effects of dark brown and white patterns, standing out clearly on a mixed brown and white ground, are obtained.

Ludigol (*m*-nitrobenzenesulphonate of soda) and picric acid both act as efficient resists under " cover " patterns printed in hydrosulphite discharges on grounds of Azoic colours or Vat dyestuffs of the Indigoid group, including Indigo itself. In this way the effect last described can be duplicated in a great variety of colours, though it is not produced in large quantities.

LUDIGOL RESERVE.

150	grms.	Ludigol.
250	,,	water.
600	,,	gum thickening 1 : 1.
1000		

Print slightly warm.

Provided the over-print or cover is not too strongly engraved, and the Rongalite or other discharge not too concentrated, this reserve acts very satisfactorily. It gives good results under the ordinary reduction discharges used for Indigo and most Azoic colours, but cannot be made strong enough to neutralise the full discharging effect of the powerful Rongalite-Leucotrope mixtures employed for Indanthrene dyeings.

Discharge Effects on Dyed Basic Colour Grounds.

White and coloured discharges are obtained on bright Basic colour grounds by means of Chlorate discharges similar to, and in some instances identical with, those used for discharging Indigo (which see). The bleached calico is padded in a 2–3 per cent. solution of tannic acid in water, then dried well and passed through a 1 per cent. solution of tartar-emetic to fix the tannin as an insoluble tannate of antimony. Thus mordanted, the cloth may be dyed in any Basic colour that is dischargeable to a white with chlorate pastes. The most easily dischargeable colours, and those most commonly used, are Auramine, Brilliant

green, Malachite green, Victoria blue, Methyl violets, and, in light shades, Rhodamine, Methylene blue, Thionine blue, Safranine and Methylene green. The list might be extended, but these colours furnish a sufficient variety for most purposes, and are capable of yielding a great number of compound shades when mixed in different proportions. The dyeing may be carried out in either a jigger or a spiral dye-beck, whichever is most convenient. Dark shades are dyed with 1–1½ per cent. of dyestuff on the weight of the cloth; light shades with ¼–½ per cent. dyestuff on a correspondingly weaker mordant. After dyeing, the goods are washed well, and are then ready for printing. A light soaping helps considerably in obtaining a good white discharge.

Any of the chlorate white discharges employed for Indigo are equally suitable for basic colours. Usually they will be found to be too strong, and must be reduced by addition of starch paste or British gum solution. For coloured discharges, pigment colours, lakes, and certain Basic and Direct colours which withstand the oxidising action of the discharge pastes are employed, with albumen as fixing agent.

The strength of the chlorate discharge determines the length of the steaming operation. With strong discharges, containing from 10–15 per cent. of chlorate, a short steaming in the rapid ager is sufficient to effect the destruction of the ground colour; with weaker discharges a more prolonged steaming—*e.g.* 15 minutes to an hour—is necessary to produce a full discharge. Generally speaking, it is preferable to employ strong discharges in conjunction with a short steaming, the reason being that the printed colours are then less liable to run, owing to the fact that they pass too quickly through the steaming chamber to absorb any appreciable quantity of moisture. At the same time it is to be noted that if the discharge pastes are stronger than is necessary for discharging the ground colour, they will cause the appearance of running whether they be steamed rapidly or slowly. Too strong a discharge, also, attacks the fibre; and in order to guard against this defect as much as possible, it is advisable to fix transverse bars of wood on the copper guide rollers in the ager, or at least wrap them with calico. Both these simple precautions prevent the cloth from coming in contact with the hot metal, and reduce its liability to become tender.

After steaming, the goods are washed well in hot water, and finally soaped and dried. Single white discharges are improved by a run through a bath of dilute caustic soda or silicate of soda at 40°–50° C.

The strength of the discharge paste must be regulated according to the depth and dischargeability of colour to be operated upon. A very suitable white discharge for general work, and one which is used extensively on the large scale, is made up as follows:—

WHITE DISCHARGE FOR BASIC COLOURS.

15	grms.	starch.
110	,,	British gum.
75	,,	China clay.
75	,,	water.
550	,,	chlorate of alumina 42° Tw.
105	,,	chlorate of soda. Boil, cool, and add—
25	,,	red prussiate of potash.

Water to 1000

For discharging a ground dyed with 1½ per cent. Victoria blue, or with 1 per cent. Malachite green, take—

1 part of the above White discharge.
2 parts British gum paste.

On a 1 per cent. Methyl violet grounding take equal parts of Discharge white and British gum paste. For deeper shades, use at full strength.

Below is given another practical recipe for a white discharge:—

WHITE C.S. 150.

{120 grms. citric acid.
{640 ,, British gum paste.

Dissolve, cool a little, and add—

150 grms. chlorate of soda.
70 ,, caustic soda 70° Tw.

Cool, and add—

20 grms. red prussiate of potash finely ground, and allow to dissolve in the cold.

1000

COLOURED DISCHARGES.

	BLUE C.	PINK C.	YELLOW C.	GREEN C.
Methylene blue	20	..	..	..
Rhodamine 6 G. extra	..	10	..	..
Chrome yellow paste	..	..	300	..
Lemon chrome yellow paste . . .	..	..	..	150
Guignet green paste	..	..	..	150
Glycerin	30	30	20	30
Acetic acid 9° Tw.	50	50	..	..
Water.	140	140	..	..
Neutral citrate of soda 46° Tw. . .	100	100	50	50
Oil (olive or rape seed)	..	..	20	20
Gum tragacanth 8 per cent. . . .	390	400	290	290
Chlorate of soda	100	100	100	100
Albumen solution 40 per cent. . .	150	150	200	190
Red prussiate of potash . . .	20	20	20	20
	1000	1000	1000	1000

The pigment colours yellow and green must be well ground in a mill before printing.

Print; steam 2–5 minutes in the rapid ager at 90° C.; wash well, and soap to clear the whites and to remove the thickening.

If the amount of chlorate in the above colours is reduced, they may be printed in combination with any ordinary steam colours on light dyed grounds. For example, in an eight-colour floral pattern on a moderately light grey or fawn ground, the pink, white, yellow, light green, and blue parts of the pattern were discharged, while the dark olive, chocolate, and black were obtained by printing ordinary steam colours. The printed goods would in such a case be steamed for ¾–1 hour, and afterwards treated as usual for chlorate discharges.

Certain basic colours are also discharged by reducing agents—*e.g.* sulphite of potash, alkaline stannous oxide pastes, and by the glucose-alkali process. Of these, the sulphite discharges alone are of practical interest, and even they are little used on account of the technical difficulties encountered in their application on the large scale. Fairly light shades of Brilliant green, Methylene blue, Azophosphine, Magenta, Malachite green, and Methylene green are all discharged by sulphite of potash. On the other hand, Auramine, Methyl violet, Victoria blue, Safranine, Rhodamine, and Phosphine resist the action of

sulphite, and may therefore be utilised for the production of coloured effects. The addition of caustic soda, however, to the sulphite of potash yields a mixture easily capable of discharging most basic dyestuffs, under the influence of steam.

SULPHITE WHITE.

500	grms.	sulphite of potash 90° Tw.
50	,,	caustic soda 77° Tw.
200	,,	water.
250	,,	British gum powder.
1000		

TYPE OF COLOUR DISCHARGES WITH SULPHITE.

20	grms.	Auramine conc.
30	,,	glycerine.
250	,,	water.
200	,,	British gum.

Boil, cool, and add—

500	grms.	sulphite of potash.
1000		

Blue = 20 grms. Victoria blue.
Pink = 10 ,, Rhodamine 6 G. extra, or Roseazine.
Green = 3 parts yellow to 1 part blue.

Print on grounds of the dischargeable colours mentioned above; steam 2–3 minutes; wash and soap.

The great disadvantage of the sulphite process is that the colours are extremely difficult to print without scumming. To some extent the effect of the scum can be counteracted by preparing the pieces in a dilute solution of chlorate of soda (½ per cent.) previous to printing; but this treatment must not be carried too far, lest the finer parts of the discharge pattern be affected also.

In the Richard process sulphite of potash is replaced by hydrosulphite-formaldehyde.

The Discharging of Direct Cotton Colours.

A greater variety of colour combinations can be obtained by discharging Direct colour grounds than by any other single discharge process. Nearly all the straightforward printed effects specially associated with particular and superior discharge styles may be, more or less successfully, *imitated in appearance* on grounds of Direct cotton colours, and many additional combinations, not practicable by other means, are easily realisable on the same type of ground. Beyond appearance, the resemblance to Indigo, Turkey-red, and Vat and Azoic colour discharge styles ceases. The great majority of the Direct-dyeing cotton colours cannot be regarded as fast, though many are fairly so, and certain of them, after development, are fast to soaping, and others are good to light. They are fast enough to form the basis of an important and popular style, and large quantities are consumed in the production of discharged patterns on dress materials of cotton and artificial silk which are not required to possess more than moderate fastness. To a less extent the Direct-dyeing colours are also used on wool and silk, and mixtures of these with cotton, for similar styles.

With certain exceptions, which are of no interest here, almost all direct-dyeing cotton colours are discharged to a more or less pure white by reducing agents. It is impossible to give anything like a complete list of the dyestuffs

suitable for this purpose—they are too numerous—but amongst the many that yield good results the following, selected from practice, occupy an important place:—

Chlorazol Fast Yellow 5 G.K.	Triazogene Orange R.
,, ,, Red K.	Chloramine Sky Blue F.F.
,, ,, Heliotrope B.K.	,, Fast Violet 2 R.L.
,, ,, Blue 2 B.	Chlorantine Fast Blue 2 G.L.
,, Browns 2 G., G.M., and M.	,, ,, Violet 4 B.L.
,, Black E.	,, ,, Brown B.R.L.
,, Drab R.H.	Chrysophenine G.
,, Brilliant Black B.X.X.	Chicago Blue, all brands.
Diamine Azo Scarlet 8 B. ex.	Diazo Fast Blue 2 R.W.
,, ,, Fast Bordeaux B.	,, ,, Black B.H.L.
,, ,, Blue 6 B.	,, Phenyl Blue 2 B.
Diazamine Blues B.R. and 2 R.	Direct Sky Blue G.S.
Diaminogene Pure Blue N.	Diphenyl Pink B.K.
Formal Black G. conc.	Parasulphon Brown V.
Oxamine Brilliant Light Blue B.	Sirius Green B.B.
,, ,, ,, Green 3 G.	,, Light Brown T.
Trisulphon Brown B.	Rosophenines.
,, Bronze B.	Naphthamine blues.

Many other colours could be mentioned, and are used extensively, but the foregoing will be sufficient to illustrate the style. They comprise a wide range of shades, and a vast number of compound shades can be produced from them at will. For ground shades fast to soaping choice must be made from those colours which lend themselves to diazotising and developing with naphthols or amino compounds; or those which are capable of coupling with diazo compounds. Diazamine and Diaminogene blues are typical of the first class, and Chlorazol browns and Pluto brown R. of the second; but scores of both groups are available and are illustrated in the pattern cards of most colour manufacturers.

Undoubtedly the best discharging agents for Direct colours are the various sulphoxylate-formaldehyde compounds—Formosul, Britulite, Rongalite, etc. —which frequently give excellent white discharges where other reducing agents are useless. Nevertheless, the tin discharges are still employed (especially for acetate silk fabrics) and will probably retain their place for some time to come.

Sulphoxylate-Formaldehyde (Hydrosulphite) Discharges.

For very dark shades of blue, green, and brown, and for Direct blacks, the discharge colours that are used for Paranitraniline red and Azoic colours generally may be used equally well for Direct colour grounds. For lighter shades, the amount of hydrosulphite must be reduced to 25–75 grms. per kilo. of colour. With this adjustment the same formulæ exactly will serve for the preparation of all white and colour discharge pastes used in the discharging of Direct dyes.

On flannelettes, for which the style is eminently adapted, an addition of zinc oxide is frequently made to the white discharge; it keeps the paste on the surface of the material and gives a better local discharge in consequence. Additions of Anthraquinone, Leucotrope W., and ammonium citrate, etc., either singly or together, are also made for the purpose of increasing the effect of the hydrosulphite in cases where the ground is difficult to discharge by ordinary means.

Coloured discharges are generally produced with Basic colours though, on

the faster grounds, Vat colours are not infrequently employed on account of their fastness. For certain classes of work pigment colours fixed with albumen are also used to some extent, notably for very bright blues made-up from ultramarine for strong shades and mixtures of ultramarine and zinc oxide for light shades.

Basic colours are fixed in different ways with tannic acid, Katanol O.N., or zinc ferrocyanide. Thus:—

(1) The dyed goods are printed with Basic colour discharges *containing* tannic acid.
(2) The goods are first padded in tannic acid mordants and then printed with colours containing *no* tannic acid.
(3) Same as (2) but prepared in Katanol O.N.
(4) The dyed goods are printed with Basic colour discharges containing zinc chloride and subsequently passed through a fixing and reoxidising bath of sodium ferrocyanide and sodium bichromate.

Each of these processes has its merits and drawbacks. The first is the most expeditious, but the colours do not keep well and are apt to work badly; in the second and third, the colours both keep better and work well in printing, but the method involves an extra process and is therefore more expensive; the last process (4) combines the advantages of the other three without their disadvantages and, moreover, yields more brilliant discharge colours which, however, are unfortunately somewhat inferior in fastness to washing.

Other methods of fixing Basic dyestuffs in discharge styles have been suggested from time to time, as for instance those based on the formation of condensation products of resorcin and formaldehyde and the coagulation of albumen or glue by formaldehyde, the formaldehyde being derived, in both cases, from the dissociation of Rongalite C., etc., during the steaming of the printed goods. None of these processes has come into general use, though the resorcin method is worthy of attention, especially when modified slightly by the addition of hexamethylenetetramine.

Discharges which are required to resist an Aniline black cover (over-print) are made, as usual, by the addition of sodium or magnesium acetate to the ordinary discharge printing pastes, with a further addition of zinc oxide to the white.

The choice of a white discharge suitable for a particular ground can best be decided by a practical trial. Most Direct colours discharge fairly easily, but not all give a good white with Rongalite or Formosul alone, and in such cases special treatment is necessary.

Hydrosulphite White Discharges.	I.	II.	III.	IV.
Flour-tragacanth paste (thick)	500	..	470	..
Gum arabic 1 : 1	..	600	..	600
Water	200	..	..	..
Formosul or Rongalite C.	100	100	80	100
Dissolve at 140° F., cool, and add—				
Zinc oxide	100	..	50	..
Water	75	..	50	..
Glycerine	25	..	..	..
Leucotrope W. conc.	..	..	30	..
Anthraquinone 30 per cent. paste	..	..	20	..
Ammonium citrate 20° Tw.	..	..	..	150
Water	..	300	300	150
Grms.	1000	1000	1000	1000

The above discharges may be reduced as required by diminishing the sulphoxylate content and, if desired, may be thickened with other materials, such as British, Karaya, Senegal, or Ghatti gum, tragacanth mucilage, or starch-tragacanth paste. In general, the presence of zinc oxide is beneficial; a portion of it is always retained by the fibre after washing and, by filling up the interstices of the cloth with solid white pigment, it adds considerably to the brilliancy of the white discharge. Small spots, trails, sprigs, etc., discharged on a pale ground with hydrosulphites alone show up very indistinctly, but if printed with discharges containing 100–150 grms. of zinc oxide per kilo. they stand out prominently.

With the foregoing discharges (I.) and (III.) reduced in strength, very fine imitations of light Indigo styles can be obtained. The blue ground is dyed with dyestuffs of the Diaminogene pure blue N. or Diazo fast blue 6 G.W. conc. type, diazotised and developed with β-naphthol. It is faster than corresponding light shades of Indigo, and is not subject to the same irregularity in dyeing.

The dyeing is carried out on a padding machine as follows:—

Light Blue D.

(1) Slop-pad the bleached cloth through—

1000 c.c.		water (boiling).
12	grms.	Diaminogene pure blue N.
30	,,	sulphate of soda.
10	,,	caustic soda 66° Tw.

Pad as near the boil as possible and dry directly over a cylinder-drying machine. The goods may now be diazotised at once or passed through the rapid ager. A short steaming improves the fastness. After cooling they pass to the operations of diazotising and developing, which are performed in a continuous manner.

(2) Diazotising and developing.—Run the goods at full width through a series of roller becks containing—

(*a*)	1000	litres	cold water.
	4	kilos.	sodium nitrite 98 per cent.
	8	,,	sulphuric acid 168° Tw.

Wash in—

(*b*) 1000 litres cold water.

(*c*) 1000 ,, ,, ,,

and develop in—

(*d*)	1000	litres	water.
	13	kilos.	β-naphthol.
	13	,,	caustic soda 66° Tw.

Wash in—

(*e*) 1000 litres water.

Afterwards wash well in the rope form and soap lightly; wash, dry, and before printing pad the dyed pieces through a ½ per cent. solution of chlorate of soda to counteract any scumming that may occur in printing. For a black and white effect on a blue ground, print an Aniline or Logwood-iron black (see Black J.) and hydrosulphite white (I.) or (III.) reduced 1 : 1, steam for 3–5 minutes, wash, soap lightly, and dry. Any sulphoxylate compound—Formosul, Rongalite C., Britulite—will give equally good results. If the combination contains Basic colour discharges the goods, after steaming, are passed through tartar-emetic (10 grms. per litre) previous to washing, etc.

Dark grounds of Direct colours are better obtained by dyeing on jiggers or

in the ordinary rope-dyeing becks. Jiggers are the more convenient unless large quantities of one shade are required.

Fine shades of the always popular Navy blues and dark browns are obtained from developed dyestuffs of the Diazamine blue B.R., Diamine azo blue 6 B., Chlorazol brown M., and Parasulphon brown V. types respectively, of each of which groups there are scores of members of every imaginable shade and hue. Two examples will serve to illustrate the general application of these dyestuffs.

NAVY BLUE D.Z. (Diazotised and Developed).

(1) Dye with—

4	per cent.	Diazamine blue B.R. (Sandoz).
$1\frac{1}{2}$	,,	soda-ash.
10–15	,,	Glauber's salt.

Raise the temperature gradually and dye for $\frac{3}{4}$ hour at boiling, adding the Glauber's salt during the course of dyeing. Wash well.

(2) Diazotise with—

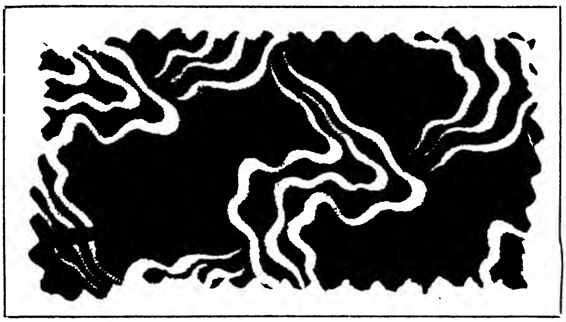
1	per cent.	nitrite of soda 98 per cent.
2	,,	sulphuric acid 168° Tw.
dissolved in sufficient water.		

Wash well.

(3) Develop in—

1	per cent.	β-naphthol.
1	,,	caustic soda 66° Tw.
cold water, a sufficiency.		

Wash, etc., exactly as for Light blue D. and prepare in a $\frac{1}{2}$ per cent. solution of chlorate of soda.



4 per cent. Diazamine Blue B.R., discharged as below (Sandoz).

WHITE DISCHARGE S.

200	grms.	Hydrosulphite R.F.N. (Rongalite C.).
100	,,	water.
600	,,	British gum 1 : 1.
20	,,	formaldehyde 40 per cent.
80	,,	citric acid 1 : 1.
1000		

Print, steam in the rapid ager, wash, soap, and dry.

Of the various dyestuffs that are developed by direct coupling with diazo bodies, the Chlorazol browns and Parasulphon brown V. are typical and popular examples.

DIRECT BROWN C. (Coupled).

(1) Dye with—

3–4	per cent.	Parasulphon brown V. or Chlorazol brown M.
$1\frac{1}{2}$	,,	soda-ash.
10–15	,,	Glauber's salt.

Wash well.

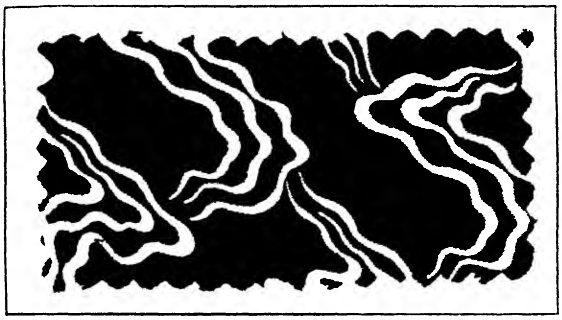
(2) Couple in—

50–70 per cent. diazo-*p*-nitraniline solution (corresponding to 10 grms. *p*-nitraniline per litre) in sufficient water.

or in—

$\frac{1}{2}$–$\frac{3}{4}$ per cent. *p*-nitraniline diazotised as for dyeing red.

Wash well, dry, and prepare in $\frac{1}{2}$ per cent. sodium chlorate solution before printing.

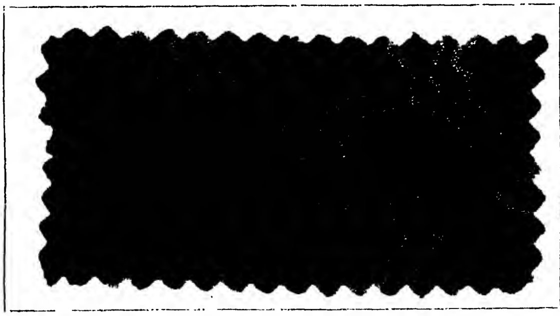


3 per cent. Parasulphon Brown V., discharged with Hydrosulphite (Sandoz).

The dyed cloth is printed with the preceding white discharge S. and treated as before. Many other white discharges containing less hydrosulphite and no citric acid are equally suitable for these two dyeings.

Basic Colour Discharges.—Generally speaking the same colour discharges that are used for Azoic colour grounds may be used also for discharging Direct colour grounds provided the sulphoxylate-formaldehyde content is reduced. As a rule, however, the two styles are kept separate, special ranges of colours being provided for each.

(1) ORDINARY METHOD.—The ordinary method of working, in which the tannic acid is mixed with colouring matter and discharging agent and the whole printed together, is illustrated by the two following patterns:—

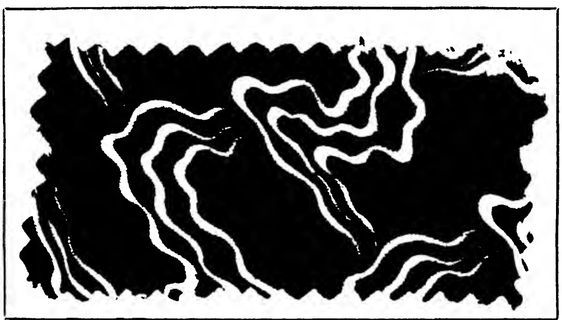


Ground: 2 per cent. Chloramine Sky Blue F.F.
Yellow discharge: Tannoflavine T. (see overleaf).
Pink discharge: Rhodamine 6 G.H. Extra (see overleaf)
(Sandoz).

Discharge Colours.

	Yellow. grms.	Pink. grms.
Gum arabic 1 : 1	330	330
Hydrosulphite R.F.N. (or Rongalite)	70	70
Formaldehyde 40 per cent.	30	30
Sodium bisulphite 67° Tw.	110	110
Aniline	80	80
Warm to 170°–190° F. and add		
Alcohol	100	100
Tannoflavine T.	30	..
Rhodamine 6 G.H. extra	..	20
Heat until all is dissolved, cool, and add—		
Tannic acid	125	125
Water	125	125
Make up to	1 litre	1 litre

Print, steam, pass through tartar-emetic (10 grms. per litre), wash, and dry.
The next pattern has been produced by the same methods on a ground of Diazamine blue 2 R. with white and orange discharges.



Dyed ground: 4 per cent. Diazamine Blue 2 R., diazotised and developed.
White: White Discharge S. 3 : 1 (see above).
Orange: Sabaphosphine O. (30 grms. per litre) (Sandoz).

Orange Discharge.

Made up like the preceding pink, but with 30 grms. Sabaphosphine O. and 120 grms. Hydrosulphite R.F.N. per litre.

Print, steam, fix in tartar emetic, etc., as already described.

All Basic dyestuffs capable of withstanding reducing agents may be applied by the foregoing method.

(2) Another interesting method of producing Basic colour discharges is based upon the simultaneous formation of zinc tannate and a resorcin-formaldehyde condensation product during the steaming operation. Both these bodies act as fixing agents for Basic colours and, before steaming, the presence of resorcin prevents the precipitation of the colouring matter by the tannic acid. In steaming, the various components of the printing mixture react: zinc tannate is precipitated and combines with the colouring matter to form an insoluble lake, and formaldehyde splits off from the Rongalite C. and combines with the resorcin to form an insoluble resinous body which acts as an additional fixative. In this way the colouring matter is completely fixed on the fibre and requires no further treatment in tartar-emetic.

The discharge colours detailed below are taken from practice—

DISCHARGE ROSE Z.R. (Zinc-Resorcin).

(a) { 325 grms. Rhodamine 6 G. ordinary strength.
500 ,, glycerine.
1000 ,, water.
750 ,, resorcin.

Dissolve and add—

5000 grms. gum arabic 1 : 1.

Heat the mixture, then cool, and add in order—

(b) { 400 grms. zinc chloride (solid).
500 ,, water.

(c) { 500 ,, tannic acid.
500 ,, water.

(d) { 500 ,, Rongalite C. 1 : 1.
500 ,, water.

Make up to 10 litres

BLUE :	As Rose, but with			250 grms.	Methylene blue S.
LIGHT BLUE :	,,	,,	,,	,,	Rhoduline blue G.O.O.
YELLOW :	,,	,,	,,	,,	Thioflavine T.C.N.
ORANGE :	,,	,,	,,	,,	Acridine orange D.H.
DARK PINK :	,,	,,		{ 300 grms. 60 ,,	Rhodamine 6 G. ordinary. Rhodamine B. extra.

Greens, violets, olives, etc., are made from mixtures of the foregoing standard colours. The amount of Rongalite C. may be reduced or increased according to the ground to be discharged.

The dyed material is printed with the foregoing colours, steamed, washed only, and dried. It is advantageous to give the steamed goods a run through a bath of bichromate of soda (2 grms. per litre) before washing, in order to accelerate the re-oxidation of the Basic colour discharges. This can be done in the open soaping machine in the usual manner.

(3) BASIC COLOUR DISCHARGES ON DIRECT COLOUR GROUNDS PADDED IN TANNIN BEFORE PRINTING.—In this process the tannic acid component of the final colour lake is applied to the dyed goods in the form of a prepare, the discharge printing colour itself consisting only of dyestuff, thickening, and Rongalite. It is a popular process in practice because, as already stated, the colours work well and are stable. They also yield very even shades in large objects, which is not always the case with colours containing tannic acid.

After dyeing to the required ground shade, the goods are washed, dried, and slop-padded in :—

TANNIC PREPARE.

{ 12·5 grms. tannic acid.
6·25 ,, chlorate of soda.
1000 c.c. water.

Then dry and print the following colours :—

DISCHARGE ROSE T.

{ 325 grms. Rhodamine 6 G. ordinary.
1250 ,, water.
500 ,, glycerine.
6000 ,, gum arabic or Ghezireh 1 : 1.

Boil, cool, and add—

{500 grms. Rongalite C.
{500 ,, water.

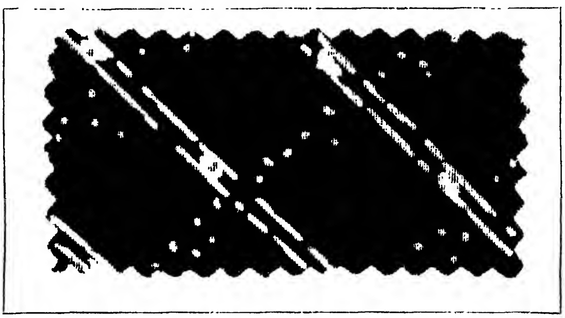
Make up to 10 litres with water or gum.

Blue T.:	As Rose, but with 250 grms.				Methylene blue S.
Light Blue T.:	,,	,,	,,	,,	Thionine blue G.O.
Yellow T.:	,,	,,	,,	,,	Thioflavine T.C.N.
Orange T.:	,,	,,	,,	,,	Acridine orange D.H.
Scarlet T.:	,,	,,	{250 grms.		Acridine orange D.H.
			{62·5 ,,		Rhodamine B. extra.

Compound shades—greens, olives, mauves, violets, etc.—can be obtained from mixtures of the foregoing standard colours, and quiet tertiary shades of grey, blue, fawn, and the like by utilising such dyestuffs as Modern grey R.C.N., Modern violet, Modern blue C.V.I., and Modern yellow N. as indicated for analogous discharges on β-naphthol colours.

After printing the foregoing series of colours on tannin-prepared cloth, the goods are steamed for 4–5 minutes in the rapid ager at 102° C., washed, chromed, washed again, and dried.

(4) Basic Colour Discharges on Direct Colour Grounds Padded in Katanol O.N. before Printing.—The only essential difference between this process and the one immediately preceding is that tannic acid is replaced by Katanol O.N.—a sulphurised phenol which forms insoluble lakes with Basic dyestuffs. Exactly the same printing colours may be used for both prepares but, as Katanol imparts a slightly yellowish tint to the fabric, and is actually dyed upon it, it is preferable to employ a discharge containing Leucotrope W. and Anthraquinone. For most purposes, however, any efficient discharges of other composition, whether white or coloured, yield satisfactory results. The formulæ given here are those by which the two examples illustrating the Katanol process have been produced.



(I.G.).

Ground: Dyed 1½ per cent. Sirius Light Brown T., padded Katanol O.N., 12/1000.
White: Rongalite C., etc. (see below).
Blue: Toluidine Blue, 10/1000.

The bleached cloth dyed with 1½ per cent. Sirius light brown T. is padded in—

Katanol Prepare.

{12 grms. Katanol O.N.
{1·2 ,, soda-ash.
{10 c.c. Monopol Brilliant Oil (optional).

Made up to 1000 c.c. with water

at about 120° F., dried, and printed with—

WHITE DISCHARGE.

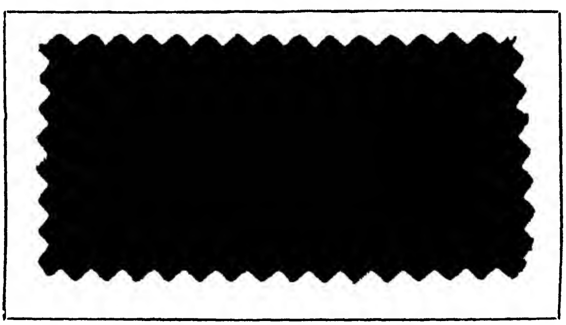
400	grms.	neutral starch-tragacanth paste.
100	,,	zinc oxide 50 per cent. paste.
80	,,	Rongalite C.
30	,,	Leucotrope W.
20	,,	Anthraquinone 30 per cent. paste.
370	,,	water or thickening.
1000		

BLUE DISCHARGE.

10	grms.	Toluidine blue.
20	,,	Glyecine A.
20	,,	Acetine N.
240	,,	water.
650	,,	gum arabic 1 : 1.
60	,,	Rongalite C.
1000		

After printing, steam for 5 minutes in the rapid ager, pass, in the open width, through a fixing bath of Katanol O.N. (2 grms. per litre) at 85°–105° F., then through a warm bath (80°–90° F.) of potassium bichromate 0·2 per cent. and, finally, wash well and dry.

In the same manner the following pattern dyed a Direct red has been prepared and printed in green and orange:—



(I.G.).

Ground: Diazo Brilliant Scarlet R.O.A. Extra.
Green: Mixture (see overleaf).
Orange: ,, ,,

GROUND.

3 per cent. Diazo brilliant scarlet R.O.A. extra, diazotised and developed in β-naphthol.

PREPARE.

Katanol O.N., as before.

Discharge Colours.

	Orange.	Green.
Euchrysine R.R.D.X.	15 grms.	..
Auramine G.	5 „	10 grms.
Rhoduline blue 3 G.	..	10 „
Glyecine A.	20 „	20 „
Acetine N.	20 „	20 „
Water	210 „	210 „
Gum arabic 1 : 1	650 „	650 „
Rongalite C.	80 „	80 „
	1000	1000

Print, steam, fix in Katanol, chrome and wash as described for the preceding example.

The Katanol process yields coloured discharges which are *faster to washing* than similar Basic colour discharges produced by other methods. The second fixing in a warm solution of Katanol O.N., after steaming, adds considerably to this quality.

(5) The Zinc Prussiate-Rongalite Process of Discharging Direct Colour Dyeings.—The idea of this process was suggested by the zinc oxide Aniline black resist style in which the fixation of Basic dyestuffs is effected by means of zinc ferrocyanide, with which they combine to form an insoluble lake. At the outset an attempt was made to work on the lines of the Aniline black process by padding the dyed goods in a solution of potassium ferrocyanide and by printing with discharge colours containing zinc oxide or various salts of zinc. So far as the discharges went the results were satisfactory, but, unfortunately, it was found that the padded cloth was exceedingly liable to contract stains of Prussian blue over large areas of its surface during the steaming process and, as it was impracticable to remove these without detriment to ground and printed colours alike, a different line of attack had to be adopted. The process was *reversed,* and no further trouble with Prussian blue was encountered. The plain dyed goods were printed with zinc salt-Rongalite discharge colours, steamed, and then fixed and re-oxidised simultaneously by a passage through a bath of sodium ferrocyanide and sodium bichromate. In its final form the process was worked as follows:—

(*A.*) The dyed goods were padded through a solution of:—

$$\left.\begin{cases}\text{62·5 grms. chlorate of soda,}\\ \text{10 litres water,}\end{cases}\right\} = \text{1 oz. per gallon,}$$

to counteract scumming or printing smears. They were then dried.

(*B.*) The discharge colours prepared according to the standard formula given below were printed.

Formula for Coloured Discharges (Z.F. Colours).

250	grms.	Basic dyestuff.
1000	c.c.	water.
500	„	glycerine.
5500	„	gum arabic 1 : 1 (or other gum).

Heat to boiling, cool, and add—

500–1000	grms.	Rongalite C.
500–750	„	water.
500	„	zinc chloride.
500	„	water.

Make up to 10 litres

The latitude in Rongalite is to provide for light and dark dyed grounds, the latter requiring a stronger discharge.

Discharge Blue Z.F.	=	250 grms.	Methylene blue S.
Discharge Light Blue Z.F.	=	„ „	Thionine blue G.O.O.
Discharge Orange Z.F.	=	„ „	Acridine orange D.H.
Discharge Yellow Z.F.	=	„ „	Thioflavine T.C.N.
Discharge $\frac{4}{1}$ Scarlet Z.F.	=	250 grms.	Acridine orange D.H.
		62·5 „	Rhodamine B. extra.

A full shade of rose or pink can be obtained only by using a fairly large amount of dyestuff, and it is preferable to prepare a special printing colour for such shades:—

Discharge Rose Z.F.

375 grms. Rhodamine 6 G. ord. (or 75 grms. 6 G.H. extra).
500 c.c. methylated spirit.
3250 „ water.

Dissolve and add a mixture of—

600 grms. maize starch.
1200 „ light British gum.
3000 c.c. water.

Boil, cool, and add—

500–1000 grms. Rongalite C.
1000 „ water.
500 „ zinc chloride.
500 „ water.

Make up to 10 litres

Rhodamine B., and the concentrated brand B. extra, are made up in the same manner. They give very blue shades of rose, inclining to violet at full strength.

Greens, violets, and other compound shades are obtained by mixing the foregoing colours in various proportions. Thus:—

Green Z.F. =	2–4 parts	Yellow Z.F.
	1–1 „	Light blue Z.F.
Olive Z.F. =	3–5 „	Orange Z.F.
	1–1 „	Light blue Z.F.
Violet Z.F. =	2–3 „	Rose Z.F.
	1–1 „	Light blue Z.F.
Mauve Z.F. =	6 „	Rose Z.F.
	1 „	Blue or Light blue Z.F.
	etc.	

Bluish pinks and reddish violets of greater fastness than those obtained from Rhodamine mixtures, and of exceptional brightness, are produced by Astra phloxine F.F. extra and Astra violet F.F.D. extra (I.G. Dyestuffs). Both these dyestuffs are rapidly destroyed by Rongalite in discharges of the ordinary composition, but in the presence of a fairly large proportion of aniline, phenol, or resorcin this destructive action is prevented or, at least, inhibited, and the colours keep sufficiently well for practical purposes. Prepared with these additions the Astra colours may be employed for discharging Direct colour dyeings either by the "tannin in colour" method, or for printing *without* tannic acid on tannin or Katanol prepare, or for application, as below, by the zinc prussiate process. Thus:—

RECIPE FOR ASTRA PHLOXINE OR VIOLET Z.F.

300	grms.	Dyestuff.
250	,,	Acetine J.
500	,,	methylated spirit.
1250	,,	water.

Dissolve and add to—

5000	grms.	British gum-starch paste	Heat together and cool to 120° F.
250– 700	,,	aniline oil.	
250–1000	,,	Rongalite C.	
500	,,	zinc chloride (neutral).	
500	,,	water.	

Make up to 10,000 c.c.

The proportion of aniline in this recipe ought not to be less than 66 per cent. of the Rongalite used.

The dyed goods, printed with the foregoing colours of the Z.F. series, are first steamed for 4 minutes at 214°–216° F. in the rapid ager and then passed through a fixing bath of:—

16 kilos.	yellow prussiate of soda	(12·5 grms.),
4 ,,	bichromate of soda	(3·125 ,,),
1280 litres of water		(1 litre),

or, more simply—

80	litres	Fixing liquor Y.P. (below).
1200	,,	water.

FIXING LIQUOR Y.P.

2000	grms.	yellow prussiate of soda.
500	,,	bichromate of soda.

in 10 litres

For every 120 metres of cloth (9–15 kilos. weight) passing through the fixing bath, replenish with about 10 litres of Fixing liquor Y.P. reduced 1 : 15 with water. After fixing, wash well and dry.

The advantages attaching to the zinc prussiate-Rongalite process consist in its cheapness, its freedom from liability to contract iron stains owing to the absence of tannic acid, and the superior purity and brightness of the coloured discharges and the brilliancy of the white discharges. The coloured discharges are slightly looser to washing than those on tannin and Katanol mordants, but they are sufficiently fast in this respect to satisfy the demands made on the Basic colour discharge styles, and their exceptional brightness has led to the extensive employment of the process in practice.

It may be mentioned that certain Basic dyestuffs which are readily destroyed by Rongalite find a place in the range of dischargeable ground shades. Amongst these the most important are Setoglaucine and Setocyanine (Geigy), Acronol brilliant blue and Victoria blue R. (I.C.I.) and, occasionally, Methyl violet 2 B. They are all dyed, in the customary manner, on tannin-mordanted cloth. Their use is restricted to the production of exceedingly bright blues and emerald greens—much brighter than anything of similar shade obtainable from direct dyeing colours—and, although they are not remarkable for fastness to light, they are indispensable for brightness, no other dischargeable dyestuffs approaching them for brilliancy of effect. The blues are dyed with Basic dyestuffs alone, whereas the bright greens are first dyed with

Chlorazol yellow 5 G.K. (on tanned cloth) and then re-dyed with Setoglaucine. The rest of the process follows the routine already described.

Coloured discharges on grounds of Direct blacks are not often printed, better results being obtained by the Aniline black resist style.

Tin Discharges.

Prior to the introduction of the hydrosulphite-formaldehyde compounds, all really practicable processes for producing discharge effects on ground shades of Direct dyes were based on the application of the reducing properties of stannous salts. The hydrosulphites are undoubtedly the reducing agents *par excellence* of the calico printer ; but in order to take the fullest advantage of their powerful action, they require to be submitted to the influence of air-free steam at a temperature only possible of attainment in specially constructed agers. On the other hand, the stannous compounds effect the decolorising of Direct dyestuffs in ordinary rapid agers, and under the ordinary conditions which obtain in those simple machines —that is, in the presence of moisture and air, and at a comparatively low temperature. In some cases even the mere drying of the printed cloth is sufficient to bring about the decolorising reaction. Hence the tin discharges are valuable alternatives to those prepared from hydrosulphites if only because they can be applied satisfactorily in circumstances and conditions unfavourable to the latter. Tin discharges do not give so pure a white as do the hydrosulphites, and, moreover, they are liable to attack the fibre. With care, however, they yield excellent results ; and for the flannelette trade, for which they are principally used, the quality of the white is usually sufficiently good to pass unquestioned.

The stannous compounds may be used either as acid salts or in the form of alkaline stannites, the latter chiefly for white discharges which are required to resist a cover print of Aniline black. The acid tin white discharges consist for the most part of stannous chloride, acetic, tartaric or citric acid, and acetate of soda, or of stannous acetate, together with organic acids, and sometimes with stannous chloride in addition. Coloured discharges of the same type are obtained generally by adding tannic acid and Basic colours to an acid tin discharge paste.

(*a*) Acid Tin Discharges.

White Discharge A.T. I.

90	grms.	starch.
380	,,	water.
100	,,	acetic acid 6° Tw.
60	,,	6 per cent. tragacanth thickening. Boil, cool, and add—
250	,,	stannous chloride.
120	,,	acetate of soda cryst.
1000		

White Discharge A.T. II.

85	grms.	starch.
450	,,	water.
100	,,	6 per cent. tragacanth. Boil, cool, and add—
25	,,	citric acid.
240	,,	stannous chloride.
100	,,	ammonium sulphocyanide.
1000		

This gives a very good white.

Both these discharge whites are suitable for a 2–3 minutes' steaming in the rapid ager. Acetate of soda and sulphocyanide of ammonia are introduced to prevent the tendering of the fibre.

Discharges for prolonged steaming may be made from the preceding by reducing the stannous chloride content to 5–7½ per cent.

Thus I. 4 parts starch paste.
1 part Discharge white A.T. I.
II. 3 parts starch paste.
1 part Discharge white A.T. II.

Discharge whites for long steaming may also be composed of acetate of tin:—

Discharge White A.T. III.

50	grms.	starch.
200	,,	dark British gum.
580	,,	acetate of tin 32° Tw.
120	,,	acetic acid 9° Tw. Boil, and add whilst cooling—
50	,,	tartaric acid (powdered).
1000		

Coloured discharges to work alongside the above are commonly obtained by adding Basic colours and tannic acid to thickened mixtures of acetate of tin and organic acids, or of stannous chloride and acetate of soda. The goods are steamed for an hour to effect the discharge, and then washed in water and soaped lightly. A run through tartar-emetic improves both the white and the fastness of the colours, but is not absolutely necessary. Blacks, chocolates, dark olives, etc., are printed in ordinary steam colours.

The following recipes are typical of those used according to this method:—

Basic Colour Discharges on Direct Colour Grounds.

Methylene blue, Nile blue, Marine blue, Auramine, Thioflavine T., Brilliant green, Rhodamine, Roseazine, Safranine, Phosphine, etc., are all suitable for coloured discharges.

General Formula.

20– 30	grms.	colouring matter.
240–230	,,	acetic acid 6° Tw.
50	,,	tartaric acid. Dissolve, and pour into—
240	,,	starch paste.

Heat for a short time, cool, and add—

100–150	grms.	50 per cent. tannin solution (in acetic acid).
350–300	,,	discharge paste C.
1000–1000		

Discharge Paste C.

400	grms.	acetate of tin 32° Tw.
120	,,	British gum.
25	,,	starch.
160	,,	water.

Boil, cool, and add whilst still lukewarm—

45	grms.	acetate of soda.
200	,,	stannous chloride.

Stir till dissolved, and then add—

50	grms.	citric acid (ground fine).
1000		

Print, steam for ¾–1 hour, fix in tartar-emetic, wash well, and soap lightly.

In working on the large scale, and especially with heavy patterns, the results obtained in this way leave much to be desired. As pointed out by one of the authors[1] some years ago, the process has several disadvantages, of which the following may be cited :—

1. The discharge colour does not always work well in printing—it is apt to stick in the engraving, and consequently gives an unsound print.

2. The shades produced are not so bright as one would expect from Basic colours.

3. The colours are not particularly fast to either hot water or soap.

The last, perhaps, is the most objectionable, for if passable colours are desired the pieces ought not to be hot watered or soaped ; and if either of these operations be omitted, the whole of the thickening and tin remains on the cloth. If the goods are merely washed in cold water the colours are " toppy," and extremely liable to mark off or smear the ground shade whilst in the wet state.

These defects are due in a large measure to the formation in the printing colour of an insoluble compound colour lake, which has therefore no chance of being fixed on the fibre, and simply adheres to it mechanically like an unfixed pigment colour. With a view to overcoming them, an improved process was suggested, which, while based upon the same principle as the older method, differed from it in the manner of applying the tannic acid. Instead of printing a discharge colour containing tannic acid on the plain dyed cloth, the latter was previously mordanted with tannate of antimony in the usual way ; then printed with a discharge consisting only of Basic dyestuff, thickening, and any suitable salt of tin ; and finally steamed, washed, and soaped.

The results obtained were superior in almost every respect to those yielded by the older process. The colours worked better, were brighter, and, as regards their fastness to soaping, were quite equal to the ordinary Basic print-on colours. The only objection to this method is, that the ground colours are very slightly dulled by the presence of tannate of antimony. This difficulty was surmounted at a later date by a modification of the process which consisted in padding the dyed cloth with tannin alone, and in adding the antimony salt to the discharge colour.

In washing, after steaming, the whole of the tannin except that combined with the discharge colour is removed from the cloth, leaving the cloth practically in its original condition before printing.

In carrying out this improved process, the directions given below may be followed :—

(1) Pad the dyed cloth in

20	grms.	tannic acid.
5	,,	chlorate of soda.
1000	,,	water.

Dry in the hot flue if possible ; if not, over cylinders, the first half-dozen of which are wrapped with calico.

(2) Print with any of the colours given below. Dry.

(3) Steam 2–3 minutes in the rapid ager.

(4) Wash well and soap.

It is advantageous to pass the printed goods through *ammonia vapour* before steaming ; and though not absolutely essential for light patterns, this operation is very necessary in cases where heavy patterns putting a lot of

[1] Fothergill: *Jour. Soc. Dyers and Colourists*, p. 17, 1899.

colour on are printed. Its object is to prevent the tendering of the fibre during steaming, and to ensure a sharply defined discharge. The beneficial action of ammonia is probably due to the formation of stannous hydrate, which, being both insoluble and in an alkaline state, can neither run nor attack the fibre.

As a rule, the run through gaseous ammonia may be omitted when the goods are steamed in the rapid ager, but it is always better to include it in the process when an hour's steaming is essential.

TIN DISCHARGE WHITE F.

250	grms.	stannous chloride.
100	,,	sulphocyanide of ammonia.
75	,,	acetic acid 9° Tw.
10	,,	1 per cent. sol. of Methylene blue.
565	,,	starch paste.
1000		

COLOURED DISCHARGES.

20– 30	grms.	basic dyestuff.
150–140	,,	water.
80	,,	acetic acid 9° Tw.

Dissolve and add to—

250	grms.	antimony paste.
500	,,	discharge paste F.
1000		

YELLOW =	Auramine conc.	(20 grms.)
BLUE =	New methylene blue N.	(30 ,,)
PINK =	Rhodamine 6 G. extra	(10 ,,)
RED =	Safranine A.N. extra	(15 ,,)
	Rhodamine 6 G. extra	(10 ,,)
	Thioflavine T.	(5 ,,)
GREEN =	Auramine conc.	(15 ,,)
	Brilliant green	(10 ,,)
VIOLET =	4 Discharge pink.	
	1 ,, blue.	
ORANGE =	Auramine conc.	(20 ,,)
	Acridine orange N.O.	(5 ,,)
	Rhodamine 6 G. extra	(2 ,,)

ANTIMONY PASTE.

120	grms.	starch.
200	,,	acetic acid 9° Tw.
600	,,	water.
80	,,	sodium antimony fluoride.
1000		Boil and cool.

DISCHARGE PASTE F.

390	grms.	thick starch paste.
50	,,	acetic acid.
400	,,	stannous chloride.
160	,,	sulphocyanide of ammonia.
1000		Stir till dissolved.

All the above colours are adapted for steaming in the rapid ager; if they are required to work in combination with steam colours the percentage of tin must be reduced. The amount of reduction will depend upon the strength of the engraving of the pattern to be printed, and also upon the intensity of the shade to be discharged. For ordinary work about 70 grammes per kilogramme of colour is ample, but heavier patterns require less, and lighter patterns more. The reduction is most readily effected by replacing part of the Discharge paste F. with starch paste.

The process known as the Richard process is, in so far as it relates to the discharging of Direct dyestuffs, merely an adaptation of the foregoing, the only difference between the two being that hydrosulphites are used in place of stannous salts.

(b) Alkaline Tin Discharges on Direct Dyes.

These discharges find but little application except for producing coloured effects with pigments, and for certain "conversion" styles. These latter, worked out by Pluzanski, are very pretty, but not very fast, and are rarely produced at the present time by this method.

For ordinary work, stannous hydrate mixed with British gum-starch paste, ammonium chloride, and a slightly alkaline tartrate of ammonia is the reducing agent employed both for white and coloured discharges.

White Discharge S.H.

350	grms.	stannous hydrate paste.
75	,,	ammonium chloride.
90	,,	British gum.
40	,,	starch.
310	,,	water. Boil, cool, and add—
135	,,	tartrate of ammonia 36° Tw.
1000		

Stannous Hydrate Paste.

{700 grms. stannous chloride.
{ 10 litres water. Dissolve, and add gradually—
{500 grms. (about) soda-ash.
{ 10 litres water.

Wash the precipitate by decantation and filter to 2000 grms.

Pigment Colour Discharges.

200	grms.	Chrome yellow.
100	,,	50 per cent. blood albumen.
690	,,	Discharge white S.H.
10	,,	turpentine.
1000		

Print, steam, wash, and soap. The tartrate of ammonia dissociates in steaming, leaving the free acid to assist in bringing about a more complete discharge of the Direct colour ground shade.

Pluzanski's process for discharging Direct colour grounds and resisting a black cover at the same time is simply an amplification of the above. The only difference between the two is that in the Pluzanski an excess of alkali, sufficient to prevent the development of the black, is employed. The process is principally

used for light shades of Direct colours; indeed, on dark shades it is impracticable, as the whole effect of a black cover would be lost if the ground were too deep. The best and most striking results are obtained on such shades as are dyed with about 1 per cent. of Erika pink, Diamine sky blue F.F., Chicago blue, Diamine green, Diamine yellow N., and Diamine brown B., etc. The following table shows the percentages of dyestuff used in dyeing some few of the many shades suitable for the style in question:—

	PINK.	BLUE.	GREEN.	FAWN.	VIOLET.	HELIOTROPE.
Erika pink	1–2	..	..	..	½	½
Diamine sky blue F.F.	..	..	..	..	..	1
„ green G.	..	..	½	..	..	..
„ yellow N.	..	..	½	½	..	..
„ brown B.	..	..	..	1	..	..
Chicago blue	..	1–2	..	..	½	..
Glauber salt	10	10	10	10	10	10
Phosphate of soda	5	5	5	5	5	5

On the above dyed grounds, the colours given below yield satisfactory results.

WHITE DISCHARGE RESIST P. I.

a
103 grms. water.
160 „ tartaric acid.
Dissolve, and add—
80 grms. 6 per cent. tragacanth.
And then sprinkle in gradually—
80 grms. soda-ash.
Stir until the reaction is finished, and then add—
200 grms. 6 per cent. tragacanth.
15 „ glycerine.
200 „ caustic soda 98° Tw.

b
102 „ stannous chloride.
60 „ 6 per cent. tragacanth thickening.

Add (*a*) to (*b*), carefully stirring vigorously all the time to prevent lumps from forming. It is well to grind the mixture before it is used for printing.

WHITE DISCHARGE RESIST P. II.

60 grms. tartaric acid.
320 „ water.
120 „ soda-ash.
250 „ British gum (well torrefied).
125 „ water.
25 „ glycerine.

Boil, cool, and add—
100 grms. stannous chloride.

1000

This white is only suitable for producing a white pattern under an Aniline black cover on a dyed ground.

Conversion effects are obtained by printing a prussiate Aniline black containing a Basic colour over White resist discharge P. I. Wherever the black

falls on the discharge it will be destroyed, leaving the Basic colour intact. For example, to obtain a four-colour effect of pink, black, green, and white, the following series of operations are gone through: –

(1) Print White discharge resist P. I. on *pink* dyed cloth in, say, a big spot pattern. Dry.

(2) Cover with a closely set oblique line pattern (a slashed line) in Aniline black containing Brilliant green.

(3) Steam 3 minutes and then wash, etc.

The ultimate effect is that of a *Green and White striped spot* on a black and pink striped ground, the black line being converted into green wherever it crosses any spot. The Basic colour is fixed by the tin ferrocyanide precipitated on the cloth, but it is only moderately fast to washing. The addition of a little tannic acid to the black, or better still, the mordanting of the dyed cloth with antimony tannate, improves the fastness considerably, but is apt to impair the density of the black.

Colour blacks for conversion styles may be made up as under:—

	Pink.	Green.	Blue.	Violet.
	grms.	grms.	grms.	grms.
Yellow prussiate of potash	60	60	60	60
Chlorate of soda	40	40	40	40
6 per cent. tragacanth	240	240	240	240
Water	250	250	250	250
Starch	50	50	50	50
Aniline salt	90	90	90	90
Aniline oil	10	10	10	10
Water	100	100	100	100
Rhodamine 6 G. extra	15	..	..	12
Auramine conc.	..	15	..	..
Thionine blue G.O.	..	5	20	4
Water	145	140	140	144
	1000	1000	1000	1000

Similar but much superior conversion effects are obtained by operating with mixtures of hydrosulphite-formaldehyde and zinc oxide, or hydrosulphite-formaldehyde, zinc sulphate, and acetate of soda, on dyed cloth previously padded in a 2 per cent. solution of zinc sulphate. Instead of the unfixed Basic colour washing out of the black parts of the pattern and staining the light dyed ground, the whole of it is fixed as a zinc ferrocyanide lake The white also is much purer, and many Direct colours can be brought into use that are not readily discharged to a good white by any form of tin discharge pastes. A better method, perhaps, is to replace the preparation of the cloth in zinc sulphate by a run through a warm solution of the same after steaming. In this way all possibility of impoverishing the Aniline black is removed.

To secure the best results with tin discharges, the utmost care should be taken to observe the following precautions:—

(1) The discharge pastes ought not to be stronger than is necessary to cut the ground shade completely. If too strong, the colours run, giving a clumsy impression; and the excess of tin salts not merely produces a white aureole round the colours, but attacks the fibre most energetically.

(2) The steaming ought to be as short as possible; and for this reason it is preferable to employ strong discharges and give a short run through the rapid ager, rather than to print weak discharges and steam for a longer period

in the continuous steamer. When this latter is unavoidable, the steam must not be too damp, otherwise the discharge colours, which are hygroscopic in character, will absorb a large amount of moisture, and swell in consequence.

(3) If the whites are yellowish, a little extra citric acid will improve them, or the goods may be soured in dilute hydrochloric acid after steaming. The longer the goods have been steamed, the yellower will the whites be; hence the advisability of a short steaming.

Properly carried out, the tin discharges are capable of giving a variety of fine effects; but they are limited to a smaller range of ground shades than the hydrosulphite-formaldehyde discharges, and consequently they have been displaced to a great extent.

Pigment Colour Discharges on Direct Colours.

The fact that hydrosulphites do not coagulate albumen allows of certain pigments and lakes being utilised for obtaining coloured effects on various Direct colour grounds. The process is not much used, though it possesses certain advantages in the way of simplicity and brightness. The colours stand out well, as all plastic substances do when printed, and they are as fast to light and soaping as any other group except the Vat colours. The Chrome yellows cannot be used on account of the blackening action of hydrosulphite; but the range is, nevertheless, a wide one, including red, yellow, blue, green, and various browns and oranges.

The printing colours may be made by simply adding 50–100 grms. of hydrosulphite-formaldehyde per kilo. of any ordinary pigment colour that will withstand the reducing action during steaming; or they may be made up according to the following type:—

Discharge Red.

100	grms.	Limol or Lithol fast red.
100	,,	water.
520	,,	tragacanth thickening.
180	,,	egg albumen solution 50 per cent.
100	,,	Formosul.
1000		

Blue = Ultramarine blue or Thionine blue G.O. lake.
Yellow = Auramine, Acridine, and other Basic yellow lakes, or cadmium sulphide.
Green = Mixtures of Basic colour blues and yellows.
Orange = Pink and Basic yellow lakes; or red above mixed with yellows.
Pink = Rhodamine lake or Eosine lakes.

A convenient method of employing Basic colours as pigments is to combine them with zinc oxide as the base, and then apply them as ordinary pigments with albumen and hydrosulphite. Thus, for example:—

Discharge Yellow.

25	grms.	Acridine yellow G.
15	,,	Acridine orange N.O.
15	,,	glycerine.
130	,,	water.
325	,,	tragacanth thickening.

Boil, cool, and add—
125 grms. zinc oxide.
240 ,, egg albumen solution 50 per cent.
125 ,, Formosul.

1000

Rhodamine 6 G., Thionine blue G.O., etc., are used in the same way for pink, blue, and other colours.

Pigment colour discharges are, after printing, simply steamed, lightly chromed, and washed.

Vat Colour Discharges on Direct Colours.

Sometimes for special purposes, as, for example, certain crimp effects, the Vat colours are employed for discharging Direct colour grounds. The discharges do not differ materially from the usual printing colours (*q.v.*), the only variation being in the addition of a little extra hydrosulphite-formaldehyde—an addition not always necessary. The following colours are typical examples of this method of working:—

	Blue.	Pink.	Crimson.	Scarlet.	Orange.
	grms.	grms.	grms.	grms.	grms.
Ciba blue 2 B. paste	150	..	..	..	..
Ciba pink paste	..	100	..	..	..
Durindone red 3 B. paste	..	..	150	..	..
Ciba scarlet G.	..	..	..	200	..
Ciba orange G.	..	..	..	..	200
Glycerin	70	70	70	70	70
Water	100	100	100	55	55
British gum thickening	520	605	505	500	500
Caustic soda 86° Tw.	70	35	70	70	70
Hydrosulphite conc. ($Na_2S_2O_4$)	15	15	30	30	30
Heat to 140° F., cool, and add—					
Formosul	75	75	75	75	75
	1000	1000	1000	1000	1000

British Gum Thickening.

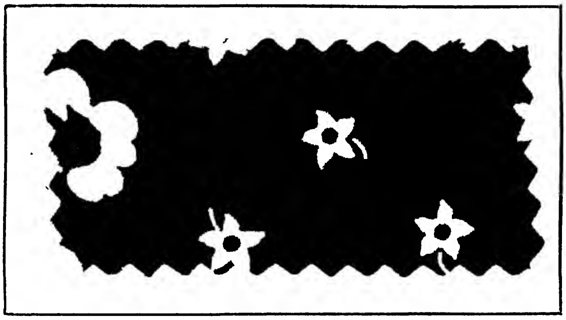
$\begin{cases} \text{170 grms. China clay.} \\ \text{150 ,, water.} \end{cases}$
375 ,, British gum.
305 ,, water.

1000

The foregoing colours are printed on suitable Direct colour grounds, *i.e.* diazotised and developed or coupled colours; then steamed for 4 minutes at 216°–220° F. in air-free steam, and finally chromed, washed, and soaped at the boil. Hot soaping is essential to develop the full beauty of many vat colours; hence the necessity for dyeing fast ground shades.

It goes without saying that the ordinary printing colours prepared from Vat dyestuffs of the Caledon, Indanthrene, Algole, and Cibanone groups are all equally applicable to the discharging of Direct colour grounds; also that carbonate of potash may replace caustic soda in most cases without detriment.

The pattern below has been printed by the Rongalite-carbonate process, and will serve to illustrate the style.



(S.C.I.B.).

Ground: 2 per cent. Diazo Fast Blue 6 G.W. conc., diazotised and developed.
Red: Ciba Scarlet G., 200 grms. per kilo.
White: Hydrosulphite R. conc. Ciba (=Rongalite C.)

The cloth, dyed, diazotised, and developed in β-naphthol, is printed with any suitable white discharge and the following red:—

200	grms.	Ciba Scarlet G. in paste form.
50	,,	glycerine.
200	,,	British gum 1 : 1.
250	,,	starch-tragacanth paste.
180	,,	carbonate of potash.
50–120	,,	Hydrosulphite R. conc. Ciba (or Rongalite C., Formosul, etc.).
1000		

Steaming, chroming, and soaping are carried out as described already.

Vat colour discharges on the faster developed and coupled Direct colour grounds have lost much of their importance since the introduction of Variamine blue, the Fast blue bases B.B. and R.R., Fast violet B. base, and the Azoic colours generally, but they are still used extensively for better-class work on cotton and artificial silk fabrics of all descriptions. Other things being equal, it is more economical to confine the execution of an order to one process than to spread it over several; hence, if an assortment of ground shades (of which some *must* be dyed with Direct colours) can be dyed satisfactorily throughout with Direct dyestuffs, it is generally so dyed, and the whole assortment afterwards printed with discharge colours belonging to a single definite series—and this even when individual colourings in the assortment could be produced in faster colours by other methods.

Discharging of Tannin Mordants.

This method of producing *white* patterns on deep, rich, Basic colour grounds is much superior to that which depends upon the application of chlorate discharges to fully dyed cloth.

It is founded upon the observation that cloth mordanted with tannate of antimony can be stripped entirely of its tannin by boiling solutions of caustic alkalies. In practice, the mordanted cloth is first printed with strong caustic soda, then steamed in the rapid ager to effect the destruction of the tannin, and finally well washed, and dyed to shade with any suitable Basic colour. The

printed parts of the material having had their mordant oxidised and dissolved out by the soda, show up as whites in the finished article, while the unprinted parts are dyed to a more or less deep shade, according to the strengths of the mordant and colouring matter employed.

PROCESS:—(1) Prepare the cloth in a 3 per cent. solution of tannic acid in a padding mangle; dry and—

(2) Fix in $1\frac{1}{2}$–2 per cent. solution of tartar-emetic, dry.

(3) Print the White Discharge given below:—

WHITE C.

500	grms.	caustic soda 77° Tw.
25	,,	glycerine.
475	,,	40 per cent. gum Senegal solution.
1000		

British gum may also be used for thickening.

(4) Dry after printing, and steam 2–4 minutes in the rapid ager.

(5) Wash well in water and dye as required. If the goods have become soiled in printing, they may be lightly soaped and washed again before dyeing.

The brightest colours and purest whites are obtained when the dye bath is slightly acidulated with sulphuric acid, or when it contains a little potash alum, tartar-emetic, and glue size. These latter additions are specially efficacious in preserving the brilliancy of the white and in enhancing the brightness and increasing the fastness, both to washing and rubbing, of the colours. Furthermore, they promote the more complete exhaustion of the dye bath.

TYPE OF DYE BATH (100 kilos. cloth).

1–2	kilos.	dyestuff.
3	,,	tartar-emetic.
$2\frac{1}{2}$	,,	potash alum.
1	kilo.	acetic acid 9° Tw.
4500–6000	litres	water.
$7\frac{1}{2}$	,,	10 per cent. solution of glue.

Dye 15 minutes in the cold; then raise within $\frac{3}{4}$ hour to the boil, and continue at this temperature for 15 minutes. Wash immediately and thoroughly; soap at 60° C. for a few minutes, and if the whites are not quite clean, give a rapid run through bleaching powder solution at $\frac{1}{4}$–$\frac{1}{2}$° Tw. Wash well again and dry.

Thickened solutions of strong caustic soda are exceedingly apt to scum in printing; and as their action on tannin mordants is very energetic, this drawback gave rise to a good deal of trouble when the tannin discharge style was first introduced. To overcome the detrimental effect of scumming, and also of doctor streaks, it is only necessary to pad the mordanted cloth in a 1–2 per cent. solution of ammonium chloride before printing. This counteracts the action of the caustic soda on tannin; and, at the strength given, it preserves the unprinted portions of the cloth from damage, while it is not sufficiently strong to affect appreciably the quality of the discharge on the printed parts. The protective action of ammonium chloride is of course due to the fact that it neutralises the caustic soda, which easily decomposes it, with the liberation of free ammonia and the formation of sodium chloride, neither of which substances has any injurious action on the mordant.

Including the several washings and dryings, and the preparation in ammonium chloride, the foregoing process involves at the least ten distinct

operations before the cloth is ready for dyeing. By mixing the ammonium chloride with the tannic acid padding solution, however, and by deferring the fixing in tartar-emetic until after the printing and steaming have been done, *four* of these operations can be dispensed with, and a notable economy effected in time, labour, and steam. The results obtained in this way, by printing caustic soda on *free* tannic acid, are, if anything, better than those obtained on tannate of antimony; the discharge, even in fine patterns, is very complete, the whites appear to be less liable to staining in the dye bath, and are therefore more easily cleared in the final washing, and the whole process is cheaper and more expeditious.

An addition of aluminium salts to the tannin mordant acts favourably on the brightness of the ultimate colour. In presence of sufficient acetic acid, the precipitate of aluminium tannate is re-dissolved, but on drying the padded cloth, it is deposited again on the fibre in its insoluble state. As a rule, a solution of tannic acid containing 30 grms. per litre is strong enough for the general run of dark shades, but it can be increased as required; and if the cloth is padded in the wet state, 50 grms. per litre will not be too much to give results corresponding to 30 grms. on dry cloth. By wet cloth is understood cloth which comes straight from the bleach-house, where it has been well squeezed to free it from excess of water, but not dried in any way.

The following details are those employed in working on the large scale:—

(1) The cloth is padded in either of these solutions:—

TANNIN MORDANTS.

I.

3 kilos. tannic acid.
1 kilo. sal ammoniac (NH_4Cl).
100 litres water.

or

2·5 kilos. tannic acid.
2·5 ,, ammonium sulphate.
100 litres water.

II.

600 grms. potash alum.
5000 ,, acetic acid 9° Tw.
20 litres water.

Dissolve, and add to—

3 kilos. tannic acid.
1 kilo. sal ammoniac.
70 litres water.

Stir till any precipitate is re-dissolved, and make up to—

100 litres.

(2) Dry, and print White C.X.

WHITE C.X.

500	grms.	caustic soda 77° Tw.
100	,,	China clay paste 50 per cent.
400	,,	40 per cent. Senegal gum solution.
1000		

The China clay is added to prevent swelling during steaming.

(3) Steam 2–4 minutes in the rapid ager.

(4) Fix in a 1½–2 per cent. solution of tartar-emetic and a little chalk. Wash well.

(5) Dye as usual, or with addition of acetic acid.

DYE BATH.

½–4	per cent.	dyestuff.
2½	,,	acetic acid.
2½	,,	potash alum.
2½	,,	tartar-emetic (optional).

NAVY BLUE	=	4	per cent.	New blue L., or 4 per cent. New fast blue R.S.
DARK PURPLE	=	1	,,	New fast blue R.S.
		1	,,	Methyl violet 6 R.
PEACOCK GREEN	=	2	,,	Methylene green.
DARK OLIVE	=	2	,,	Acridine yellow G.
		1	,,	New fast blue R.S.
CRIMSON	=	1½	,,	Methyl violet 6 R.
MYRTLE	=	¾	,,	Auramine conc.
		1½	,,	New fast blue R.S.

Brighter and lighter shades are dyed with varying quantities of Rhodamine, Setocyanine, Marine blue, Brilliant green, Auramine, etc. New fast blue R.S. and Auramine mixtures must be dyed at a temperature not exceeding 80° C.; at higher temperatures they decompose.

HALF DISCHARGES ON TANNIN.—Two-tone and white effects are obtained on cloth prepared in tannic acid by printing, along with White C. or White C.X. (caustic soda), a thickened solution of either sodium carbonate, sodium silicate, sulphite of potash, or of a mixture of stannous chloride and potassium sulpho-cyanide. Of these, sulphite of potash is the best. It gives very regular work, and clean bright half discharges on 3–5 per cent. tannin mordants. After printing, the goods are steamed, fixed in tartar-emetic, washed and dyed, as already described. The caustic soda destroys the tannin completely, while the sulphite, alkaline carbonate, etc., only discharge it partially, so that on dyeing, a two-colour and white effect is obtained.

Print on cloth padded in a 4 per cent. solution of tannic acid a two-colour pattern in White C.X. and Half discharge K.S., steam 2–4 minutes, fix in tartar-emetic (2 per cent. solution), wash well, and dye up in any desired Basic colour.

HALF DISCHARGE K.S.

600	grms.	potassium sulphite 90° Tw.
200	,,	British gum (dry).
100	,,	water.
100	,,	China clay paste 65 per cent.
1000		

A good half discharge is also given by soda-ash (150 grms. per kilo. of colour), but it is apt to be irregular in working, and the same may be said of the other substances used for the same purpose. Potassium sulphite itself does not always give satisfactory results, but it is much more reliable than the rest of the half-discharging agents, and is therefore generally preferred for this style of work.

When Aniline black is to be associated with white and half discharges, the cloth is best mordanted with tannate of antimony before printing: Aniline black does not develop well on free tannic acid, and is, moreover, not particularly successful on tannate of antimony, unless the cloth has been *soaped* and well washed before it is printed. Black and white designs on Basic colour grounds are often, therefore, executed by the chlorate discharge process.

VAT COLOUR DISCHARGES ON TANNIN MORDANTS.—The production of Vat colour discharges on tannate of antimony mordants, known to-day as the "Vat-Tannic Style," was proposed first by Tigerstedt, many years ago, though probably many of his contemporaries were struck by the same idea since, to a practical calico printer, the process is an obviously logical development or extension of the white discharge process. The original process, however, was

defective, and never came into use. Working on similar lines to Tigerstedt, but ignorant of his results, Caberti, Roggieri and Barzaghi published in the *Revue générale des matières colorantes*, 1907, a process of their own, based upon the application of Vat and Sulphur dyestuffs in strongly alkaline solution. These workers found that, although these colouring matters were sufficiently well fixed in the ordinary way of working, they formed a tannin-antimony lake, and that, in order to decompose this lake and to eliminate the tannin, it was absolutely essential to increase the proportion of reducing agent, a point which had escaped the observation of Tigerstedt.

The sulphoxylate-formaldehydes give excellent discharge effects, and glucose also yields excellent results. Stannous oxide, too, may be used, but in this case certain defects are developed by reason of the printing rollers becoming soiled.

The following are typical recipes recommended by Caberti, Roggieri and Barzaghi:—

Typical Recipes.

	Blue.	Yellow.
Indanthrene blue R.S.	200 grms.	..
Indanthrene yellow G.	..	150 grms.
Glucose 52° Tw.	150 ,,	120 ,,
Alkaline paste	650 ,,	680 ,,
British gum 50 per cent. paste	..	50 ,,
	1000	1000

Alkaline Paste.

100 grms. British gum powder.
900 ,, caustic soda 77° Tw.

1000

Glucose is not the best reducing agent for the great majority of the Indigoid and Vat dyestuffs, a much better yield and brighter shades being obtained from the sulphoxylates. On cloth prepared with tannate of antimony and sulphate of ammonia (to counteract scumming), the colours tabulated below give good results when worked according to the process indicated.

Sulphoxylate-Caustic Discharge Colours.

	Red.	Blue.	Yellow.	Violet.	Green.
	grms.	grms.	grms.	grms.	grms.
Ciba scarlet G. paste	200	..	..	..	..
Indanthrene blue R.S. paste	..	150	..	..	..
Caledon yellow G. 200 paste	..	..	75	..	15
,, brilliant purple 2 R. 200 paste	..	..	..	75	..
,, jade green X. 200 paste	..	..	..	..	60
Rongalite C. or Formosul	60	75	75	75	75
Water	100	100	150	150	150
Alkaline thickening	590	625	650	650	650
Glycerine	50	50	50	50	50
	1000	1000	1000	1000	1000

Pad the bleached cloth in a three-bowl padding machine, giving two immersions, through the following solution :—

TANNIC ACID BATH.

12·5–25 grms. tannic acid.
1000 c.c. water.

Dry and fix by padding again through—

FIXING BATH.

6–12·5 grms. tartar-emetic.
25–25 ,, ammonium sulphate.
1000 c.c. water.

(25 grms. ammonium sulphate must always be used.)

Dry, *without previous washing*, either in hot air or over cylinders. If the tanned goods are fixed in the usual way with tartar-emetic and chalk and *washed before* drying they will require to be re-padded in ammonium sulphate or ammonium chloride before printing. Ammonium sulphate is the better anti-scumming agent, as it does not dissociate on copper drying cylinders, and thus avoids the formation of copper stains (tannate) which so frequently disfigure light Basic colour grounds. The variation in the strength of the tannic acid and fixing baths is to allow for variations in the depth of the dyed grounds ; light grounds dyed on a strong mordant are more often than not irregular in shade, and for such grounds it is advisable to reduce the tannic acid to a minimum, as little as 6·25 grms. tannic acid per litre being sufficient for many light and medium shades.

The goods mordanted, fixed, and dried as described, are printed with any of the foregoing sulphoxylate caustic discharge colours and, thereafter, steamed for 3–5 minutes in the rapid ager in air-free but not too dry steam at 212°–216° F., re-oxidised, and washed off at 140° F. The re-oxidation of the reduced vat colour discharges may be effected (*a*) by hanging overnight or for 24 hours, (*b*) by chroming in 1 per cent. acetic acid and 0·1 per cent. bichromate of soda for 2 minutes at 140° F., (*c*) by treating for 10 minutes in a cold 1 per cent. solution of sodium perborate, or (*d*) simply by washing in a copious supply of cold running water. The perborate treatment gives the best and most consistent results and, unlike the chroming process, leaves the mordanted ground unstained. Whichever method be adopted the goods are afterwards washed well, soaped at 130°–140° F., and washed again. The leuco compounds of the discharge colours are now completely re-oxidised and fixed, and the cloth is free from alkali and ready, without drying, for dyeing in the customary manner with Basic colours, alum, glue, and tartar-emetic.

EXAMPLE OF DYEBATH.

	I.	II.
Basic dyestuff . . .	1–4 per cent.	1–4 per cent.
Glue size	..	10 ,,
Aluminium sulphate . .	2½ ,,	..
Tartar-emetic . . .	2½ ,,	3 ,,
Acetic acid 9° Tw. . .	2½ ,,	5 ,,

calculated on the weight of the goods.

The dyestuff (dissolved in water) is added in portions during the first quarter of an hour's dyeing. The goods are dyed in the cold for 15 minutes, the temperature is then gradually raised to 195° F. and the dyeing continued for ¾–1 hour, without actually boiling. After dyeing, the goods are thoroughly washed in a rope washing machine, soaped lightly if necessary to brighten the

colours, finally being cleared by a passage through a dilute solution of sodium hypochlorite and dried directly on steamed cylinders.

The same colours printed on cloth simply padded in tannic acid give equally satisfactory results. After printing, they are steamed 2 minutes, fixed in a 2 per cent. solution of tartar-emetic containing 5 grms. ammonium chloride per litre, and then treated exactly as above.

As might be expected, the Indigoid vat dyestuffs are equally as suitable as the Indanthrenes for discharging tannin mordants. They are applied in practically the same way and are generally preferred because they give brighter effects. They are not all quite so fast as the Indanthrenes, but, as they are immeasurably faster in every way than the grounds upon which they appear, their slight inferiority in this respect is of no moment. If it were not that by this method only is it possible to obtain an extensive range of brightly coloured discharges on brilliant grounds, such as are only yielded by the Basic colours, it would be considered bad practice to associate two groups of colours so widely different in permanence as the Vat and Basic colours. To a great extent the same remarks apply to other discharge styles, in many of which either the ground or the illuminating colours fade, or wash out, long before the rest of pattern.

Vat Colour Discharges on Tannin Mordant: dyed 2 per cent. Setocyanine (Geigy).

Resists under Tannin Discharges.—If the action of caustic soda is to be counteracted (or resisted), as, for instance, in the case of a discharge white cover thrown over a basic colour ground, a portion of which ground has to be reserved so as to form a pattern, the best resisting agent to use is nitrate of ammonia thickened with starch.

Resist N.A.

I. { 335 grms. nitrate of ammonia cryst.
 665 ,, starch paste.

1000

or

II. { 2050 grms. nitric acid 57° Tw.
 1000 ,, ammonia 25 per cent. (Sp. gr. 0·910).

Add the acid to the ammonia until the solution is neutral, and then pour the whole into

350 grms. starch.
100 ,, water.

3500

Boil and cool.

Print either of the above resists on tannate of antimony prepared cloth; dry, and cover in White C.X. (caustic soda); dry, steam, wash, and dye up in basic colours. If printed on cloth prepared in tannic acid alone, the goods are passed through tartar-emetic *after* steaming; they are then washed and dyed as usual.

Very pretty and useful effects, consisting of a two-colour pattern in solid white and solid colour standing out clearly from a delicately figured ground, also in white and the same colour, are obtained by printing on tannin-mordanted cloth (1) a design in White C.X. and Resist N.A., and (2) a fine cover pattern in White C.X., the cover, of course, being printed over the whole of the first design. Thus—

Dark Blue and White Spots on a Dark Blue and White Striped Ground.

On tannate of antimony mordant—

(1) Print a two-colour spot pattern in White C.X. and Resist N.A. Dry.
(2) ,, fine closely-set line stripe in White C.X. Dry.
(3) Steam for 2–4 minutes.
(4) Wash, soap lightly, wash, and dye up in—

$$\begin{cases} 2 \text{ per cent. Victoria blue B.,} \\ 2\frac{1}{2} \text{ ,, ,, alum,} \\ 2\frac{1}{2} \text{ ,, ,, tartar-emetic,} \end{cases}$$
and a little glue size.

Wash well, soap, etc. In this way, by varying the patterns, covers, and dyestuffs, an immense variety of effects can be produced by very simple means.

Discharging of Aluminium, Iron, and Chromium Mordants.

The production of white discharges on aluminium and iron mordants has been dealt with in connection with the Madder Style, and needs no further mention here. The discharging of chrome mordants is similar in most respects, and in many cases precisely the same ingredients may be used; indeed, the majority of the acids given for Madder mordants yield equally good results on chrome mordants.

The cloth may be mordanted with either the alkaline chrome mordants of Koechlin or Knecht, the Gallois mordants, or with chromium bisulphite. With the Gallois mordants good whites are easily obtained by a short steaming, as the discharge is printed on before the chromium oxide is fixed on the fibre. With the other alkaline mordants, a more prolonged steaming is necessary to bring the hydroxide into solution.

Dark Gallois Mordant.

Chrome mordant Ga. II. 64° Tw.	200 grms.
Water	715 ,,
Glycerine	35 ,,
Gum tragacanth 6 per cent.	50 ,,
	1000

Pad the cloth in this solution; dry in the hot flue and print on the following Discharge white:—

Discharge White C.K.

85	grms.	citric acid.
75	,,	tartaric acid.
100	,,	China clay 50 per cent. paste.
740	,,	British gum paste.
1000		

Heat till dissolved and then cool.

After printing, steam the goods for 4–5 minutes, and then pass at once at full width through a 3 per cent. solution of soda-ash at 50°-60° C. Wash well and dye in any suitable mordant dyestuff. This method of working is well adapted to the production of white patterns on dark-dyed grounds.

For "two-tone and white" effects a somewhat different procedure is adopted. The cloth is first padded twice (for levelling purposes) through the following weak mordant:—

Light Gallois Mordant (Mordant G.L.).

Chrome mordant Ga. II. 64° Tw.	100 grms.
6 per cent. tragacanth thickening	50 ,,
Water	850 ,,
	1000

The excess of liquor is expressed by the bowls of the padding mangle, and then, *without drying*, the cloth is passed at once through a second padding mangle, the box of which is charged with a 3-4 per cent. solution of soda-ash at 75°-90° C. Following this, the goods are well washed, and then dried for printing. On cloth fully mordanted in this manner a discharge white and a stronger mordant are printed, and after steaming (to effect the discharge and the fixation of the strong mordant), the goods are thoroughly washed and dyed up in Alizarin, Cœruleïn, Persian berries extract, or any other mordant dyestuff that forms a pleasing chromium lake.

White Discharge T.T.

15	grms.	citric acid.
12	,,	tartaric acid.
150	,,	China clay paste 50 per cent.
823	,,	gum Senegal solution 50 per cent.
1000		

Dark Mordant for Printing.

400	grms.	Chrome acetate 32° Tw.
600	,,	thick starch-tragacanth paste.
1000		

Print on cloth prepared as above in Mordant G.L.; steam for 1 hour in the continuous steamer; pass at full width through a 1 per cent. soda-ash bath at 60° C. to ensure the complete fixation of the dark mordant; wash thoroughly in water, and then dye as under:—

For 50 Kilos. Cloth.

Claret:—

2500	litres	water.
$1\frac{1}{2}$	kilos.	Alizarin 20 per cent. (blue shade).
5	,,	10 per cent. glue solution.
1	kilo.	acetate of lime 32° Tw.
1	,,	acetic acid 9° Tw.

Dye $\frac{1}{4}$ hour in the cold, then raise the temperature gradually during $\frac{3}{4}$ hour to 90°–100° C., and dye at this temperature until the shade is fully developed.

Wash well, soap, and clear the whites in weak bleaching-powder solution or in the chloring machine.

TERRA-COTTA :—	As for Claret, but	1½ kilos. Alizarin orange 20 per cent., and no acetate of lime.
BROWN :—	As Terra-cotta, but	Anthracene brown.
BLUE :—	,, ,,	Alizarin blue S.
PURPLE :—	,, ,,	Gallein or Gallopurple.
OLIVE :—	,, ,,	Cœruleïn S.
OLD GOLD :—	,, ,,	Persian berry extract.
YELLOW :—	,, ,,	Alizarin yellow G.G.
BRIGHT VIOLET :—	,, ,,	Chromoglaucine V.M.
GREY :—	,, ,,	1 part Chromoglaucine V.M. 1½ parts Alizarin yellow G.G.
BRIGHT BLUE :—	,, ,,	Alliance blue.

The quantities of the above colours must be varied according to the shade required and to the amount of dark mordant on the cloth.

Phosphate of chromium is a much weaker mordant than the hydroxide—that is, it gives lighter colours than the latter with the same quantities of dye-stuff. On this fact is founded a method of producing very fine half-discharge effects on strong chrome mordants. A good mordant for the purpose is made up and applied as follows :—

CHROME MORDANT F.

I.	110	grms.	Formosul.
	1000	,,	water.
II.	200	,,	bichromate of potash or soda.
	200	,,	acetate of soda.
	2000	,,	water.

Add I. to II. in the cold immediately before use, and make the whole to 4 litres with water. Pad the cloth in this solution, dry in the hot flue, steam 4 minutes, and then pass through a boiling 2 per cent. solution of soda. Wash well, dry, and print Discharge white Z. and Half discharge P.S.

DISCHARGE WHITE Z.

300	grms.	citric acid.
150	,,	China clay paste 50 per cent.
550	,,	British gum paste.
1000		

HALF DISCHARGE P.S.

150	grms.	sodium phosphate (Na_2HPO_4).
850	,,	British gum paste.
1000		

After printing, run twice through the rapid ager, wash well, and dye in any of the mordant dyestuffs already given. The phosphate of chromium dyes up a lighter shade than the unprinted ground mordant, and thus yields half-discharge effects which, when associated with Aniline or Diphenyl black and White discharge Z., give useful four-colour styles on a deep rich ground of subdued colour.

It is needless to add that the chrome mordant discharge style ranks with the fastest and highest class of printed goods.

Ashton's Chrome Mordant.—The chief drawback to the use of chrome mordants in cotton dyeing was the difficulty of fixing, on the fibre, sufficient chromium hydroxide to yield a full shade on dyeing. This difficulty was overcome in the process patented by F. Ashton and the Calico Printers'

Association, Ltd. (English Patent 117715, 1918). The process is based on that originally proposed by Horace Koechlin [1] and consists essentially of passing the cloth, first, through a solution of a chromium salt and then through an alkaline bath to precipitate the chromium as an insoluble hydroxide on the fibre. It was necessary in the older process to maintain the alkaline bath at the boil, whereas in the newer the fixation is performed at the ordinary temperature. The main difference between the two, however, lies in the amount of chromium hydroxide fixed from salts containing the same percentage of chromium oxide. In Ashton's process a much larger amount is deposited on the fibre than by Koechlin's, with a corresponding increase in the depth of shade obtained on dyeing. Moreover, a single mordanting is sufficient to produce, by Ashton's process, a depth of shade that could only be obtained by repeated treatments in the older process ; consequently it is not only a better method of working, but a more economical one.

The process is carried out on an ordinary preparing machine as follows :—

1. Pad in chrome alum solution (or chromium sulphate) at 16° Tw., and dry.
2. Pad again through caustic soda 20°-40° Tw.
3. Steam (or not, as desired), batch, and allow to lie for ½ hour at least to complete the fixation.
4. Wash and dry (if for printing).

Or alternatively in a padding mangle :—

1. Pad in chromium sulphate 16° Tw. ; batch.
2. Pad again, straight through the nip, in caustic soda 40°–80° Tw.
3. Steam (without previous drying), batch, and allow to lie 30 minutes.
4. Wash and dry ; if the goods are to be dyed a plain shade, the drying may be omitted.

The steaming may take place either before or after the goods have been allowed to lie after the caustic soda treatment, or it may be dispensed with entirely. In the opinion of the inventor, however, steaming for a short time, at either stage, has a beneficial effect on the fixation of the mordant and yields superior results.

Nelson and Rouse's Process for Discharging Tannates of Iron, Alumina, and Chrome.—The inventors of this process, which was patented in conjunction with the Calico Printers' Association, Ltd., made the interesting observation that caustic soda was capable of discharging alumina, iron, and chromium mordants when these bodies existed on the fibre in the form of tannates. That tannate of alumina is dischargeable under these conditions is not surprising, but that they operate similarly, and equally well, in the case of the corresponding iron and chromium salts constituted a new and important discovery. The solvent action of caustic soda is not affected by the methods by which the tannates are fixed upon the fibre ; in some instances even the tannic acid may be mixed with the caustic soda, and printed thus, on ordinary iron, alumina, and chrome mordants, without impairing the final results, though obviously this procedure is somewhat irrational considering the properties of the substances in question and cannot be of more than limited application.

For obtaining coloured discharges, which resist subsequent dyeing operations, the caustic discharge is mixed with Vat or Sulphur colours. Strongly alkaline solutions of aluminate of soda and plumbite of soda are also applicable for the production of red and yellow discharges, the discharge effects being

[1] *A Manual of Dyeing* (Knecht, Rawson and Löwenthal), C. Griffin & Co., Ltd.

dyed and developed by the customary methods in use for such styles. If necessary, too, reducing agents such as the hydrosulphites may be utilised, in the same way, for special purposes; and any, or all, of the foregoing discharge mixtures may be printed along with Aniline black and the insoluble Azoic colours. It is evident therefore that the process, quite apart from its incontestable novelty, is of great practical value inasmuch as it lends itself to the production of a great variety of new effects—effects which combine richness and brightness of colour with the greatest fastness attainable by dyeing.

The examples given below illustrate a few of the simpler applications of Nelson and Rouse's process. By printing Azoic colours on naphtholated and mordanted cloth; by adding colouring matters to the caustic discharge; by covering in Aniline black; by a combined discharge of caustic soda and a reducing agent printed on a grounding of, say, several mordants and on Azoic red or claret; and by numerous other modifications of the process in question it is possible to produce an almost illimitable variety of colour combinations.

Example I.—

1. Mordant the fabric in chrome by Ashton's process (*q.v.*).
2. Tan by dyeing in 5–10 per cent. tannic acid at 180° F. for 1 hour; wash and dry.
3. Print any of the customary alkaline discharges; age, and wash as usual for madder mordants.
4. Dye up with any appropriate dyestuff, *e.g.* Alizarin, Persian berries, Modern blue C.V.I., or other Chrome colours.

Example II.—

1. Slop-pad in a solution containing $2\frac{1}{2}$ per cent. tannic acid and 0·625 per cent. chlorate of potash; dry and re-pad in basic acetate of iron $1\frac{1}{2}$° Tw. Then, after drying again, print and dye as in Ex. I.

Example III.—

1. The fabric is printed with a mixture of the two following thickened solutions A and B, and afterwards dried:—

   (A) 1000 c.c. acetic acid 12° Tw.
   1000 ,, acetate of iron 32° Tw.
   6000 ,, starch-tragacanth thickening.
   25 grms. Formosul.

   (B) 1000 c.c. acetic acid 12° Tw.
   6000 ,, starch-tragacanth thickening.
   1000 ,, liquid tannin 50° Tw.

2. The goods are then aged, washed, and soaped, and subsequently printed with the alkaline discharge and dyed as in Ex. I.

Example IV.—

1. Slop-pad the fabric in tannin and chlorate of potash as described in Ex. II.; then print a two-colour pattern with thickened solutions of acetates of alumina and iron (red mordant and black or purple mordant respectively), the pattern chosen covering the entire surface of the fabric. Then, after ageing, washing, and soaping, print the alkaline discharge and proceed as in Ex. II. The result is a discharge effect on a two-colour ground.

It is, of course, possible in any of the above examples to print two or more discharge colours simultaneously with either Aniline black or a diazo body; or the diazo body may form part of the ground in combination with the iron, alumina, and chrome mordants, the discharges then receiving a suitable addition of hydrosulphite for the purpose of destroying it where printed.

Example V.—
1. Prepare the fabric in β-naphthol.
2. Print a three-colour all-over pattern in Paranitraniline red, acetate of iron, and a basic sulphate of chrome.
3. Age, dung, wash, and dye in 10–15 per cent. tannic acid ; wash.
4. Print caustic soda discharges containing 25 per cent. Formosul ; age at 220° F. in air-free steam, wash, and dye in dinitroso-resorcin ; wash and clear.

The result is a white or coloured pattern on a ground consisting of red, green, and brown.

Discharging of Slop-padded Chrome Shades.

In this method of obtaining discharges on coloured grounds, the dyestuff and its mordant (chrome) are applied together, and the formation and fixation of the colour lake is effected by steaming. The fixation of the lake may be prevented by printing on the padded cloth, before steaming, certain pastes which contain either organic acids or their alkali salts, oxalate of antimony, sulphite of potash, or oxidising agents. These latter, which are practically restricted to the chlorate discharges, may, as a rule, be applied with equally good results, either before or after steaming.

The padding solutions contain, in addition to dyestuffs and mordant, certain solvents—*e.g.* soda, borax, glycerine, oleine, etc.—which promote the even impregnation of the cloth and the production of level shades. In light shades most colours of the Alizarin group are sufficiently well discharged (in reality resisted) by organic acids, antimony oxalate, tartrates, citrates, and sulphite of potash, together with citrate of ammonia. On the other hand, dark shades (with the exception of Alizarin reds and pinks) can only be discharged to a satisfactory white by means of chlorate of soda ; and colours containing the natural vegetable dyestuffs require the chlorate discharge whether they be dark or light.

In the following formulæ, all the colours are readily dischargeable with chlorate pastes in either white or colours, and most of them will also give fairly good results with citric acid, etc., if they are reduced to light shades by the addition of water.

	Terra-cotta.	Brown.	Blue.	Green.	Purple.
Alizarin orange 20 per cent. .	100	..	..	..	..
Anthracene brown 40 per cent.	..	50	..	..	..
Alizarin blue S. (powder) .	..	..	30	..	..
„ viridine F.F. . .	..	..	..	35	..
Modern violet . . .	..	..	..	..	60
Borax	20	20	..	..	..
Water	780	845	820	740	768
6 per cent. tragacanth thickening	50	50	75	50	50
Chromium acetate 32° Tw. .	50	35	75	75	120
Acetic acid	..	..	..	100	..
Hydrosulphite-formaldehyde .	..	..	..	..	2
	1000	1000	1000	1000	1000

A useful series of colours is obtained by mixing the four following standards in various proportions according to the principles described in the section on The Preparation of Compound Shades (p. 435) :—

SERIES S.P.

	Elements.			
	1. Red.	2. Yellow.	3. Blue.	4. Green.
Chrome violet	50	..	..	..
Anthracene yellow powder	..	12	..	..
Alizarin blue S. powder	..	..	30	..
„ green paste	..	..	..	90
Water	750	858	845	810
Acetate of chrome 30° Tw.	150	80	75	50
6 per cent. tragacanth	50	50	50	50
	1000	1000	1000	1000

Grey,	1.3.9.9	Plum,	3.0.1.1	Dull t'cotta,	1.3.0.0
Iron grey,	1.8.1.3	Reddish purple,	8.0.1.0	Russet,	1.6.1.0
Holland,	0.20.1.0	Stone,	0.20.0.1	Lavender,	1.1.1.1 (dilute)
Drab,	0.8.1.0	Reseda,	0.8.0.1	Buff,	1.40.0.1 (dilute)

Bright olives of all descriptions are easily obtained from the above three elements, red, yellow, and blue, by the addition of a green made from Alizarin viridine, instead of Alizarin green, which is dull and blue in tone.

Pad the foregoing solutions on bleached cloth ; dry and print on the discharge pastes ; steam for from $\frac{3}{4}$ to 1 hour ; wash well and soap, etc., as for Alizarin colours in general.

Chlorate discharges, when printed in combination with steam colours, must not be so strong as to attack the fibre during the steaming process. A discharge containing 40–50 grms. of chlorate of soda per kilogramme of colour is about the usual strength for most classes of work, but it is increased or diminished according to circumstances.

If the padded cloth be steamed for an hour to fix the colour lake, and then, after washing and soaping (or without these operations), it be printed with chlorate discharges, these latter may be much stronger, because the cloth then only requires a short steaming (3–5 minutes in the rapid ager) to effect the discharge alone, the colour being already fixed by the previous steaming. If, however, steam colours form any part of the printed pattern, they will require a prolonged steaming for their proper fixation ; and any chlorate discharges, therefore, that are worked in combination with them must be reduced in strength to 40–50 grms. per kilo., for the reason given above, and also because, in long steaming, smaller quantities of chlorate act quite as effectually as the larger quantities employed when the goods are merely passed through the ager.

Under any conditions of steaming, the employment of too strong a discharge is to be avoided on both technical and economical grounds ; for, apart from waste of material, the excess of chlorate, etc., over that required to discharge the colour acts on the work injuriously in two ways, neither of which can be remedied. In the first place, it attacks and tenders the fibre ; and secondly, it gives a rough, smudgy-looking, clumsy impression of the pattern, due either to the discharge running or to the too copious evolution of chlorine compounds, which naturally attack those portions of the ground colour immediately surrounding the printed pattern.

Indigosol Discharges on Chrome Colours, Etc.—In virtue of their excellent resistance to the powerful oxidising action of an amount of chlorate of soda greatly in excess of that required for their normal development, a few of the Indigosol dyestuffs lend themselves admirably to the production of bright and very fast discharges on grounds of Chrome colours—and also, it may be noted, on grounds of various Sulphur colours and dark Indigo.

Chlorate discharges on these several grounds have hitherto been restricted to the use of pigment, lake, or Basic colours, or to Azoic colours, none of which is entirely satisfactory. The first three groups give discharges of inferior fastness to soaping, rubbing, and light, whereas the Azoic colours (on Indigo and Sulphur colour dyeings), though of good general fastness, are limited to the production of yellow, orange, and red effects and, in addition, require a previous preparation of the cloth with a naphthol, which precludes the possibility of printing simultaneously a satisfactory chlorate white.

On the other hand, the Indigosols give bright yellow, orange, red, pink, violet, and green discharges of excellent fastness, and the nature of the process allows of a good white being obtained without the slightest difficulty. The printing colours possess better stability than the Azoic colour discharges, though like all colours prepared with chlorates they must not be made up too long in advance.

Only the following Indigosols are suitable for chlorate discharges:—

Indigosol yellow H.C.G.	Indigosol red H.R.
,, orange H.R.	,, green I.B.
,, pink I.R.ex.	,, red violet I.R.H.
,, scarlet H.B.	

Discharge Colours.

	Yellow. grms.	Orange. grms.	Pink. grms.	Red. grms.	Green. grms.
Indigosol yellow H.C.G.	100	..	..	..	40
,, orange H.R.	..	80	..	..	..
,, pink I.R.	..	..	40	..	..
,, scarlet H.B.	..	..	..	84	..
,, red H.R.	..	..	..	16	..
,, green I.B.	..	..	..	..	60
Water	110	130	170	110	110
Starch-tragacanth paste	220	220	220	220	220
Indigosol developer D.	60	60	60	60	60
,, ,, G.A.	50	50	50	50	50
Dissolve; when lukewarm add—					
Chlorate of soda (powdered)	200	200	200	200	200
Cool completely and add—					
Yellow prussiate of potash	60	60	60	60	60
Starch-tragacanth paste	190	190	190	190	190
Ammonia 25 per cent.	10	10	10	10	10
	1000 grms. each				

The proportions indicated above are suitable for dark Indigo dyeings and Chrome colour pads. For lighter grounds the oxidising agents must be reduced according to the depth and dischargeability of the ground shade in hand. A good white discharge is as follows:—

WHITE CHLORATE DISCHARGE.

(A) = 800 grms.	80	grms.	wheat starch.
	480	,,	water.
	192	,,	chlorate of soda.
	Boil, cool and add—		
	48	grms.	yellow prussiate of potash.
(B) = 200 grms.	50	,,	tartaric acid.
	50	,,	citric acid.
	100	,,	water.
	1000		

Process.—Print the foregoing discharges on dark Chrome colour grounds or dyeings of Indigo and Sulphur colours, steam for 5 minutes in the rapid ager at 212°–215° F., pass for 2–3 minutes through a bath of silicate of soda (5 grms. per litre) at 180°–195° F., wash well, and dry. Very dark grounds of Indigo, or any ground difficult to discharge, may be steamed twice for 5 minutes.

The Indigosol discharges are employed chiefly for the always popular and important "Foulard Blue" style, though applicable of course to any dischargeable Chrome mordant dyestuff. Navy blues closely resembling Indigo, but somewhat redder in shade and brighter, are obtained by padding Modern blue C.V.I., Gallo navy blue G.G.D., or Chrome blue B.M.I.

NAVY BLUE PADDING LIQUOR.

700	c.c.	water.
30	grms.	Modern blue C.V.I., etc.
10	,,	formic acid 50 per cent.
75	,,	tragacanth mucilage (65 : 1000).
3	,,	Rongalite 1 : 1.
80	,,	chromium acetate 32° Tw.
To 1000 c.c.		

Pad, dry in the hot flue, steam for 5 minutes in the rapid ager, and then, without washing, print the chlorate discharges and proceed thereafter as already described.

In many cases it is possible to print the goods immediately after padding and without previous steaming. If that is done it is advisable to steam the goods *twice* after printing, in order to ensure the complete fixation of the blue ground.

Other chlorate discharges already given for Indigo and the Basic colours are equally suitable for application to the slop-padded chrome shades. If necessary, they may be strengthened by the addition of more chlorate and corresponding quantities of citric acid and yellow prussiate, or they may be reduced by the addition of more thickening paste.

Other Discharges on Chrome Colours.—Other discharges used for light shades are given below:—

WHITE A.

200	grms.	citric acid.
100	,,	China clay paste 50%.
700	,,	gum Senegal solution.
1000		

WHITE B.

150	grms.	oxalate of antimony.
170	,,	British gum powder.
680	,,	water.
1000		

WHITE C.

100 grms.	oxalate of antimony.
65 ,,	tartaric acid.
100 ,,	China clay paste 50%.
735 ,,	British gum paste.
1000	

WHITE D.

150 grms.	British gum powder.
600 ,,	sulphite of potash 91° Tw.
50 ,,	China clay (dry).
200 ,,	citrate of ammonia.
1000	

Print on padded, but unsteamed, chrome shades; dry, steam 1 hour, wash well, soap well, and clear in the chloring machine with bleaching-powder solution $\frac{1}{4}°$–$\frac{1}{2}°$ Tw.

Sulphite Discharges.—Brown shades obtained from alkaline solutions of dinitroso-resorcin are discharged by means of sulphite of potash. (Binder's process.)

The cloth may be padded as under:—

DARK BROWN.

I.	100 grms.	Dinitroso-resorcin 40 per cent. paste.
	50 ,,	borax.
	350 ,,	water.
II.	60 ,,	ammonia 25 per cent.
	5 ,,	Turkey-red oil 40 per cent.
	200 ,,	water.

Mix I. and II., stir well, and add—

25 grms.	alkaline copper solution.
100 ,,	water.
50 ,,	6 per cent. tragacanth.
60 ,,	water.
1000	

ALKALINE COPPER SOLUTION.

400 grms.	copper chloride cryst.
600 ,,	water.
500 ,,	tartaric acid.
1060 ,,	caustic soda 86° Tw.
400 ,,	glycerine.

LIGHT BROWN.

25 grms.	Dinitroso-resorcin 40 per cent. paste.
40 ,,	borax.
250 ,,	water.
5 ,,	Turkey-red oil 40 per cent.
100 ,,	water.
30 ,,	chromium acetate 30° Tw.
25 ,,	alkaline copper solution.
50 ,,	6 per cent. tragacanth.
475 ,,	water.
1000	

Pad the cloth in the above solutions, dry, and print on the following discharges:—

WHITE D.R.

{200 grms. British gum.
{450 ,, sulphite of potash 90° Tw.

Heat to 50° C., stir until dissolved; then cool, and add—

150 grms. China clay paste 50 per cent.
100 ,, bisulphite of soda 64° Tw.
100 ,, citrate of soda 50° Tw.

1000

COLOURED DISCHARGES.

	BLUE D.R.	YELLOW D.R.	RED D.R.	GREEN D.R.
Dianil blue H. 6 G.	30	..	..	7½
Aurophenine O.	..	30	..	22½
Dianil fast scarlet 4 B.S.	..	..	30	..
Water	410	410	410	410
British gum powder	220	220	220	220
Sulphite of potash 90° Tw.	290	290	290	290
Bisulphite of soda 64° Tw.	50	50	50	50
	1000	1000	1000	1000

After printing, steam the goods for an hour in the continuous steamer, and then wash well and soap lightly.

Dinitroso-resorcin is put on the market under various trade names—Fast myrtle, Solid green O., Alsace green, Resorcin green—but all the products they designate are practically the same, and can be applied according to the method described above.

Discharges on Dinitroso-resorcin brown grounds have little to recommend them beyond their scientific interest. The ground shade itself is dull compared with Para brown, and the discharge colours are neither particularly fast nor bright.

Discharging of Sulphur Colours.

The ever-increasing importance of this group of colouring matters has naturally led to many attempts being made to produce white and coloured discharge effects upon grounds dyed with them. Of these attempts the most successful and convenient is that based upon the employment of powerful oxidising agents, and in this connection the chlorate discharges may be regarded as the best. Very few of the Sulphur colours yield good whites, even with chlorate, and only then when the discharge is very strong. For imitations of such goods as men's suitings, a dull white is perhaps more useful than a pure white, but for most styles the impossibility of obtaining a perfectly pure white discharge on Sulphur colours is a fatal defect in the process. The colours are easily destroyed by the chlorate pastes, but unfortunately they form brownish or greyish oxidation products, which, in the majority of cases, cannot be removed entirely from the fibre. This drawback, as already noted, is of little moment for certain classes of work, but in the main it has resulted in the chlorate discharge process being discarded in favour of the newer, simpler, and more generally applicable Zinc Chloride Resist process, which allows of the production of a much greater variety of styles, and is, moreover, free from the serious risk common to all acid oxidation discharges, namely, that of tendering the fibre.

For white discharges on medium and light shades, and for coloured dis-

charges in general, the chlorate pastes given for Indigo and Chrome colours may be used satisfactorily for the Sulphur colours. For dark shades and blacks, the following aluminium chlorate discharge gives good results, especially in fine patterns. Large patterns are not suitable, as the impurity of the white shows up to greater disadvantage in proportion as the contrast between ground and pattern is diminished.

WHITE DISCHARGE.

150 grms. British gum.
600 ,, chlorate of alumina 42° Tw.
50 ,, China clay (optional, but useful sometimes).

Beat the clay to a cream with the chlorate, and then heat the whole to 75°–80° C. and add—

150 grms. chlorate of soda. Dissolve, cool, and add—
50 ,, red prussiate of potash (powdered).

1000

For pigment colour discharges the above white may be utilised thus:—

DISCHARGE YELLOW.

300 grms. Chrome yellow paste.
150 ,, albumen solution 40–50 per cent.
525 ,, White discharge.
25 ,, citrate of ammonia 50° Tw.

1000

Guignet green, vermilion, the ochres, lakes, etc., may be used in a similar way for other colours and compound shades.

Print the white and colour discharges on cloth dyed with Sulphur colours; dry and steam for 5 minutes in the hydrosulphite ager at 100° C.; wash well and soap at 80°–90° C. for 5 minutes; then wash again and dry. To obtain the best results, the cloth ought to be well soaped before printing. If the pattern consists of white alone, or in combination with Aniline black or a Logwood iron black, the goods are passed, after steaming, through a bath of dilute caustic soda (10 grms. NaOH 77° Tw. per litre) at 60° C., followed by soaping, etc. This treatment improves the white considerably, but if applied to pigment colour discharges it is apt to strip them off the fibre.

The dyeing of the cloth may be effected by any of the usual methods in use for Sulphur colours. Particulars of the processes will be found described in *A Manual of Dyeing*, by Knecht, Rawson, and Loewenthal.

Discharging of Mineral Colours.

(a) Iron Buff.

This colour simply consists of ferric oxide, and, while very fast to light and boiling alkalies, it is extremely sensitive to the action of acids, which dissolve it out completely. To obtain white discharges, therefore, it is only necessary to print the dyed material with an acid, give a short steaming to increase its effect, and finally wash the goods in a copious supply of running water. Citric acid is most commonly used for the purpose, and usually a little oxalic acid is added to help in reducing the ferric oxide to the ferrous state. The addition of oxalic acid, however, while beneficial, is not absolutely necessary, as good whites are regularly obtained with citric acid alone. The iron is not precipitated from citrates by alkalies, and consequently a run through dilute

ammonia or soda, *after steaming*, is permissible in order to neutralise the excess of acid on the fibre, and thus prevent it from acting upon those parts of the buff ground that are contiguous to the printed pattern.

The cloth is dyed by padding in a solution of ferrous acetate 9° Tw. (which see), followed, after drying, by a passage through a solution of caustic soda 4° Tw. at 75° C. to precipitate ferrous hydrate. The goods are now allowed to lie exposed to the air for a short time (or they may be passed *at once* through a dilute solution of bleaching powder) to convert the ferrous into ferric hydrate, and then they are thoroughly washed and dried in readiness for printing.

WHITE DISCHARGES.

I.	II.	III.		
100	250	350	grms.	citric acid.
10	10	15	,,	oxalic acid.
890	740	635	,,	British gum paste (or Senegal gum).
1000	1000	1000		

Print on Iron buff-dyed cloth, dry, steam 3–5 minutes in the rapid ager, pass through dilute ammonia, and then thoroughly wash and dry.

According to the depth of the buff is the strength of the discharge ; deep shades require a stronger discharge than light ones.

(*b*) **Prussian Blue.**

The dyeing of Prussian blue was formerly an important branch of the calico printing industry, but since the introduction of basic Aniline blues it has fallen into almost total disuse in modern printworks.

Dyed in the usual way, Prussian blue consists of ferric ferrocyanide $[Fe_4\{Fe(CN)_6\}_3]$; and although it is produced on a basis of Iron buff, its behaviour towards acids and alkalies is exactly the reverse of that colour. Prussian blue is fast to acids, whereas alkalies, and even boiling soap solutions, decompose it at once, leaving brown ferric hydroxide on the fibre.

Hence by printing thickened solutions of caustic soda, or alkaline carbonates, on cloth dyed with Prussian blue, a buff pattern on a blue ground is obtained. To convert this buff pattern into a white pattern, it is only necessary to sour the goods in dilute mineral acid, which dissolves out the ferric hydroxide without affecting the blue ground.

The most reliable method of obtaining level shades of Prussian blue on piece goods is first to dye the cloth a deep shade of Iron buff, and then precipitate the blue upon it by a run through an acidulated solution of yellow prussiate of potash (ferrocyanide). Wash well and dry.

$$\underbrace{2Fe_2(OH)_6}_{\text{Iron buff.}} + \underbrace{3K_4Fe(CN)_6}_{\text{Yellow prussiate.}} + 6H_2SO_4 = \underbrace{Fe_4\{Fe(CN)_6\}_3}_{\text{Prussian blue.}} + 6K_2SO_4 + 12H_2O$$

The following process, based on these lines, is used on the large scale :—

(1) Pad the cloth in acetate of iron 18° Tw. Dry.

(2) Steam 2 minutes.

(3) Pass through caustic soda 4° Tw. at 75° C. Allow to lie ½ hour, and then wash in water until the last trace of ferrous hydrate (olive tint) has been oxidised to ferric hydrate (bright buff). Then—

(4) Pass through the developing bath :—

20	grms.	yellow prussiate of potash.
15	,,	sulphuric acid 168° Tw.
1000	,,	water.

(5) Wash thoroughly and dry.

Dyed in this way, the cloth is then printed with buff discharge, and, if desired, a prussiate Aniline black.

BUFF DISCHARGES.

	I.	II.	III.
Caustic soda 77° Tw.	300	..	300
Soda ash	..	150	..
China clay paste 50 per cent.	200	200	..
Gum Senegal 50 per cent.	500	650	600
Water	..	..	100
	1000	1000	1000

Print, dry, and wash off at once in plenty of running water, and at the full open width to avoid marking off.

If Aniline black is also printed, the goods are passed through the rapid ager before washing, and the cloth is best prepared with a little tartaric acid in order to counteract the action of the caustic soda on the black. In fact, the padding of the cloth in a 2 per cent. solution of tartaric acid is advisable in any case, since alkaline printing colours are exceedingly liable to scum badly.

To convert the buff obtained as above into a white, the goods, after washing, are treated in sulphuric acid 2°–4° Tw. at 20°–30° C. This may be done in the rope state, and it is continued until the discharge is sufficiently white.

The chief precaution to observe in the discharging of Prussian blue is to avoid allowing the wash water to become too alkaline from the caustic soda it extracts from the printed goods. This is best prevented by conducting the earlier stages of the washing in open-bottomed becks fitted with an arrangement of spirt pipes, between which the cloth is made to pass by means of suitably adjusted guide rollers. The jets of water from the spirt pipes play on the cloth with considerable force and wash it thoroughly, the waste water escaping through the bottom of the beck and carrying the caustic soda with it. In this way all risk of the alkali accumulating in the beck, to the injury of the blue ground shade, is eliminated.

(*c*) **Chrome Green.**

Chrome green is simply hydrated oxide of chromium fixed on the cloth by any of many methods of mordanting cotton with chromium salts. As a self colour it is of no importance at the present time, although formerly it was largely employed for light shades of a quiet and very fast green. Being in reality a chrome mordant, it is discharged by methods identical with those employed for, and described under, Chrome Mordants.

(*d*) **Manganese Bronze.**

Manganese bronze or bistre consists of hydrated peroxide of manganese produced on the fibre ; it is very fast to acids, alkalies, and soap, but is easily destroyed by acid reducing agents, which convert it into soluble manganous salts.

On this property of reducing agents is based the method of producing white and coloured effects on a ground of manganese bronze. The discharging agent employed is stannous chloride in conjunction with tartaric acid.

The cloth is dyed as follows:—

(1) Pad the goods through manganese chloride ($MnCl_2$) at 72° Tw. Dry.

(2) Pass through cold caustic soda 25° Tw. Squeeze out the excess and pass again through caustic soda 10°–12° Tw.

(3) Wash well, and treat in bleaching powder solution 2° Tw. until the manganous hydrate is completely oxidised to the dark brown manganic hydrate, then wash well and dry.

This process gives a dark, rich brown, which contrasts well with the patterns discharged upon it. If desired, the process can be shortened by adding the bleaching liquor to the caustic soda bath.

Coloured discharges can be prepared either from mineral colours, vegetable colours, or the basic Aniline colours. The recipes given below will illustrate the general principle of preparing typical discharge pastes.

DISCHARGE WHITE M.N.

400 grms. water.
150 ,, light British gum.
130 ,, tartaric acid. Boil, cool, and add—
320 ,, stannous chloride 120° Tw. (60 per cent. $SnCl_2.2H_2O$).

1000

STANNOUS CHLORIDE 120° Tw.

960 grms. tin crystals ($SnCl_2.2H_2O$).
640 ,, water.

1600 = 1 litre

DISCHARGE BLUE M.N. (PRUSSIAN BLUE).

Standard:—
605 grms. water.
37·5 ,, yellow prussiate of potash.
100 ,, starch.
60 ,, British gum.

Boil, and add in order—
120 grms. tartaric acid.
60 ,, oxalic acid.
68·5 ,, "nitrate of iron" 90° Tw. [40 per cent. $Fe_2(SO_4)_3$].

1051·0, or 1000 when finished and cold.

For printing take:—8 litres Discharge blue standard M.N.
2 ,, stannous chloride solution 120° Tw.

10

DISCHARGE YELLOW M.N.

Standard:—
550 grms. water.
200 ,, lead nitrate.
150 ,, light British gum.
150 ,, tartaric acid.

1050

Boil and cool.

For printing:—7½ litres Yellow standard M.N.
2½ ,, stannous chloride solution 120° Tw.

10

Discharge Green M.N.

5	litres	Yellow standard M.N.
$2\frac{1}{2}$	,,	Blue standard M.N.
$2\frac{1}{2}$	,,	stannous chloride solution 120° Tw.
10		

Print the above colours on Manganese bronze dyed cloth; dry gently at as low a temperature as possible to avoid tendering the fibre, and then hang the goods in a cool chamber for a few hours. During the hanging the stannous chloride reduces the bronze (hydrated peroxide of manganese) to manganous oxide, which dissolves in the acid present, forming the soluble tartrate, which, in turn, is subsequently dissolved and washed out of the cloth, leaving a white or coloured pattern as the case may be. After the goods have hung sufficiently long to allow of the ground colour being completely discharged, they are taken down and washed thoroughly in a large volume of running water flowing freely through the washing machine; they are next treated in chalk and water (15–20 grms. chalk per litre) and then chromed in a 1 per cent. solution of bichromate of potash at 40°–50° C. to develop the blue, yellow, and green. Finally, wash well and dry.

Before the advent of the Coal tar colours, the above yellow, blue, and green, together with a Brazil wood pink, were practically the only colours available for discharges on Manganese bronze. The basic Coal tar colours, however, allow of a much greater variety of effects being obtained, and much brighter shades.

Basic Colour Discharges on Manganese Bronze.

Standards.	Blue.	Red.	Pink.	Yellow.	Green.
New methylene blue N.	25	..	..	..	..
Rhodamine 6 G. extra	..	25	10	..	..
Auramine O.	..	5	..	..	..
Thioflavine T.	..	..	..	20	..
Brilliant green	..	..	..	..	13
Auramine G.	..	..	..	..	20
Acetic acid 9° Tw.	175	170	175	175	175
Tartaric acid	100	100	100	100	100
Water	190	50	105	155	142
6 per cent. tragacanth	100	100	140	100	100
Starch	100	100	120	100	100
Tannic acid solution 50 per cent.	160	300	200	200	200
	850	850	850	850	850

For printing:— $\begin{cases} 850 \text{ grms. above standards.} \\ 150 \text{ ,, stannous chloride (crystals).} \end{cases}$

1000

Dissolve in the cold.

Print on Manganese bronze dyed cloth; dry and hang for a few hours; wash in running water; give a chalk bath to neutralise the last traces of acid, and then wash again and dry. The various washings are best carried out at the full open width of the cloth, to avoid marking off.

In common with other mineral colour discharge styles, the Manganese Bronze Style has declined in importance. At the present time it is produced in very small quantities, if at all, its place having been taken by the newer discharge and resist processes on coupled Chrysoïdine-paranitraniline browns and Paramine, respectively.

RESIST OR RESERVE STYLES.

The resist or reserve styles, like the discharge styles, relate to the production of white and coloured patterns on variously coloured grounds. The difference between the two classes of work is not so much one of appearance as of process, for in many cases the appearance of a resist print is identical with that of a discharge print. In discharge printing, the discharging agent is applied to the cloth *after* it has been mordanted or dyed, whereas the distinguishing feature of resist printing is, that the reserving agent or resist is printed on the cloth *before* it undergoes any process of mordanting or dyeing. A discharging agent acts by destroying compounds that are already fixed (either wholly or in part) on the fibre, while a resist acts by preventing the fixation of a colour or mordant.

Resisting agents may be divided into two great classes—mechanical and chemical resists. The former consist, for the most part, of fats, resins, and plastic substances like China clay, zinc oxide, and the sulphates of lead and barium, and are used chiefly for the production of the older, coarser, and perhaps more decorative classes of dyed work, in which breadth of effect and variety of tone in the white are of greater importance than the sharp, crisp definition of the pattern, and the brilliant and even, but often somewhat harsh, purity of the whites that are so much admired in modern work. The chemical resists include many classes of chemical compounds—*e.g.* acids, alkalies, oxidising and reducing agents, and neutral salts—and are applicable to many colours which are difficult, and even impossible, to discharge successfully when once they are fully developed on the fibre.

Nearly every class of colouring matter is capable of being resisted in one way or another; and as each class possesses different properties, the nature and composition of the various resists required differ according to circumstances. At the same time it is possible to prepare double and triple resists which are effective under two or three totally different groups of colours; and in the "two-blue, white, yellow, and green" Indigo resist style, reserve or resist pastes are used which, when printed upon light Indigo-dyed cloth, play the double rôle of discharges for the light blue, and of resists to the fixation of a darker blue which is applied to the cloth in a second run through the dye vat after printing.

Resists under Dyed Indigo.

White and coloured resist effects are produced under dyed Indigo by printing the resist pastes on white cloth, and subsequently passing the goods through, or dipping them into, the Indigo vat until the desired depth of blue is attained.

The most perfect and even resists are obtained on cloth which has been previously prepared in a thin solution of starch and afterwards cold calendered. The addition of a little copper nitrate or sulphate, nitrate of ammonia, or manganese sulphate increases the attraction of the cloth for Indigo, and has a favourable effect upon the production of dark blue shades. The beneficial

influence of calendering is due to the flattening of the threads and fibres of the material—an advantage which allows of the resist paste forming a more perfect protective cover than if the threads were left projecting.

The resist pastes most commonly employed consist essentially of soluble salts which possess oxidising properties, and are fixed on the fabric by means of thickenings sufficiently tough and elastic not to chip off or crack during the subsequent dyeing operations. In order to prevent running, and at the same time take advantage of mechanical obstruction to the penetration of the dye liquor into the fibres of the printed parts of the material, it is usual to add to the reserve pastes such solid plastic substances as lead sulphate and China clay.

The salts, oxidising and otherwise, which suggest themselves as most suitable for resist pastes are those of an acid character or of which the metallic bases are precipitated as gelatinous hydroxides by the alkali in the dye bath. Of these the nitrates, sulphates, chlorides, chromates and acetates of copper, zinc, lead, and manganese have all been proved by experience to yield good resists under Vat dyestuffs. Copper, lead, and zinc salts form together the basis of most resist pastes, manganese salts being used but rarely, and then only for special styles. The precipitated hydroxides render the pastes still more insoluble and impervious and, at the same time, their formation, by neutralising the alkali of the dye liquor which is in immediate contact with the printed resist paste, brings about the precipitation of a layer of insoluble dyestuff on the surface of the paste—a layer which itself acts as an additional resist.

The protective action of resist pastes is due partly to their oxidising properties, which have the effect of throwing out of solution regenerated dyestuff before its soluble leuco compound can reach the fibre; partly to the mechanical obstruction offered by the thickening materials, plastic bodies, resins, fats, etc., in the pastes; and partly to the afore-mentioned mixed layer of hydroxides and dyestuff which is precipitated as an insoluble crust or deposit on the surface of the pastes during the dyeing operation and inhibits effectually the penetration of the dye liquor.

In printing *fine* patterns by machine the use of China clay and lead sulphate is avoided as much as possible, since they are apt to stick in and fill up the engraving, and so give an imperfect result; but for heavy patterns, and for block work, the addition of solid plastic bodies is a great advantage; and if a brush furnisher is used in printing on the machine, all danger of sticking-in is done away with.

Single white resists may or may not contain lead salts, but if they are intended to work in combination with yellow, orange, or green resists, they must, of course, be free from lead salts, otherwise, during the chroming operation for the development of the yellow, orange, or green, the white itself would be converted into a yellow by the formation of lead chromate.

By the addition of diazo solutions to lead-zinc resist pastes, it is possible, by printing on cloth prepared in β-naphthol, to obtain very bright, fast, red, pink, and orange resists.

To ensure good results in roller printing the engraving must be deep and uniform throughout the whole pattern, and a brush furnisher is indispensable if the resist contains China clay or lead sulphate.

The resists may be printed on simple white cloth, calendered cloth, or cloth which has been previously starched and calendered. The last mentioned is the best, especially for artificial Indigo and the modern Vat dyes like the Ciba colours, etc.

The following are a few of the starch prepares that have been found suitable in practice:—

	I.	II.	III.	IV.	V.
Wheat starch	20	15	20	15	25
Glue solution 10 per cent. .	150	150	150	200	150
Water	830	810	827·5	783	775
Ammonium nitrate . .	..	..	2·5	..	..
Copper sulphate	..	..	..	2	..
Turkey-red oil 40 per cent. .	..	25	..	..	50
	1000	1000	1000	1000	1000

Pad the goods through any of the above starch prepares, and then, after drying, pass them between the bowls of a three-bowl cold calender.

On the starched and calendered cloth, print any of the resist pastes given below:—

White Resist I. (Dark Blue Ground).

150 grms. copper sulphate.
60 ,, lead acetate.
400 ,, water.

Heat until the precipitation of the lead is complete, and then add—

190 grms. water.
90 ,, flour.
60 ,, British gum. Boil, cool, and add—
50 ,, copper nitrate 80° Tw.

1000

Resist White II. (Dark Grounds).

200 grms. China clay paste 50 per cent.
100 ,, 40 per cent. gum Senegal solution.
80 ,, sulphate of copper (powdered).
90 ,, acetate of copper (powdered).
65 ,, flour.
30 ,, British gum.
335 ,, water. Boil, and add—
30 ,, tallow } previously melted together.
20 ,, resin }

Turn off steam and add—

50 grms. sulphate of alumina (powdered).

1000 Cool, and grind in a mill before use.

White or Yellow Resist III. (for Dark Grounds).

75 grms. copper sulphate (powder).
75 ,, copper acetate (powdered).
250 ,, water.
250 ,, lead sulphate 50 per cent. paste.

Heat together, and when the copper salts are in solution add—

35 grms. acetate of lead.
35 ,, nitrate of lead.

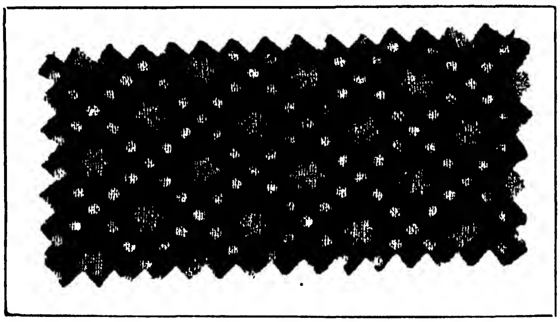
Stir the whole together at intervals during 12–24 hours, and when the lead salts are precipitated add—

30	grms.	tallow.
250	,,	30 per cent. gum Senegal solution.
1000		

Boil for one hour, replace the water that has evaporated, and then cool and grind in a mill.

YELLOW RESIST IV.

200	grms.	copper sulphate.
180	,,	lead nitrate.
520	,,	water. Boil together, cool, and add—
80	,,	flour.
20	,,	olive oil.
1000		Boil and cool; grind before using.



(H. & C.)

White and Yellow Resists under dyed Indigo.

Each of the foregoing recipes contains solid matter (insoluble lead sulphate or China clay), and is suitable for either block work, if made a little thinner, or for heavy patterns printed by machine. For thin but deeply engraved line patterns and fine spots, the two following recipes are more suitable, since they contain no insoluble bodies, and therefore do not stick in the engraving of the printing roller:—

	WHITE V.	YELLOW OR WHITE VI.
Nitrate of copper 80° Tw.	100	90
Acetate of copper cryst.	90	50
Sulphate of copper cryst.	90	..
Lead nitrate cryst.	..	200
Water	560	550
Flour	80	80
British gum	50	30
Olive oil	30	..
	1000	1000

For medium and light Indigo blues the following resist is a good one:—

White Resist VII. (for Light and Medium Grounds).

$\left\{\begin{array}{lll} 200 & \text{grms.} & \text{British gum (dark).} \\ 450 & ,, & \text{water.} \\ 50 & ,, & \text{soft soap.} \end{array}\right.$

Boil, cool, and add—

150	grms.	zinc sulphate cryst.
75	,,	nitrate of copper 80° Tw.
75	,,	thick flour paste.
1000		

After printing, the goods are hung in a warm room to harden the resist paste. They are then dipped in the Indigo vat as many times as are required to produce the desired depth of blue. After this they are treated in different ways according to the colours in the pattern.

Simple white resists are well washed, and soured for 3 minutes at 50° C. in dilute sulphuric acid (25 grms. H_2SO_4 168° Tw. per litre), and then thoroughly well washed again and dried. If required, the lead sulphate may be entirely removed by a run through boiling dilute caustic soda, but this, as a rule, is not necessary.

For white and yellow (or orange) effects the goods are printed, for white, with Resists II. or V., and for yellow, with Resists I., III., IV., or VI. After dyeing, they are washed and soured as above; then washed again, and passed for 2–3 minutes through a cold solution of lime water ($2\frac{1}{2}$ grms. lime per litre); washed, and the yellow developed by a run through the following chrome bath:—

$\left\{\begin{array}{lll} 5 & \text{grms.} & \text{bichromate of soda.} \\ 5 & ,, & \text{hydrochloric acid 4° Tw.} \\ 1000 & ,, & \text{water.} \end{array}\right.$

The chrome is maintained at a temperature of 40° C., and the speed of the goods is so regulated that they receive an immersion of 5 minutes. This treatment gives *bright lemon-yellow and white effects* on cloth printed as above. If *white and orange* reserves are required, the cloth is further treated for 1 minute in the following orange bath at the boil:—

Orange Bath:—	10	grms.	bichromate of soda.
	100	,,	caustic soda 90° Tw.
	900	,,	water.
	1 litre		

Wash well and dry. All the washing, souring, and chroming operations are conducted at the open width and in a continuous manner.

From the fact that Chrome yellow forms the basis for the production of Chrome orange, it is obviously impossible to obtain reserve effects in which these two colours appear side by side. When, therefore, yellow and orange have to be printed in combination, a yellow other than lead chromate must be employed. The yellows that come into consideration in this connection are those of the direct dyeing group, which are capable of withstanding the process of vat-dyeing and the subsequent operations of washing, souring, etc., etc. Thioflavine S., Fast Diamine yellows A., B., and F.F., Aurophenine O., Diphenyl chlorine yellow G., and Oxamine yellow 3 G. all fulfil these conditions, and have proved to be specially suitable for such work. Thioflavine S. and Oxamine

yellow 3 G. give a brilliant sulphur or lemon yellow, the Fast Diamine yellows B. and F.F. and Diphenyl chlorine yellow G. give yellow-gold shades, while Fast Diamine yellow A. and Aurophenine O. give full golden yellows, sufficiently distinguishable from the pronounced reddish tone of Chrome orange. Fast Diamine yellow B. is very soluble, and possesses remarkable fastness to light and washing—qualities which render it perhaps the most suitable of the group to employ. At the same time the others yield good results, and the redder shades especially are suitable for the production of olives by superposition on light Indigo.

Resist Yellow VIII.

50	grms.	Fast Diamine yellow B.
180	,,	British gum paste.
770	,,	White Resist II.
1000		

Heat until the colouring matter is dissolved and then cool.

For a white, yellow, and orange effect print:—

For the white —Resist White II.
,, yellow—Resist Yellow VIII.
,, orange—Resist Yellows III., IV., or VI.

After printing, hang in a warm place; dye blue, wash, sour, wash, and then chrome and orange as already described.

There are several modifications of the simple Indigo Resist Style. Of these the most important are the following:—

Style 1.—Dark Indigo, white, yellow, and orange patterns on a light Indigo ground.

Style 2.—Light Indigo, white, yellow, orange, green, and olive patterns on a dark Indigo ground.

Style 3.—White, green, and yellow patterns on dark Indigo.

Style 4.—Multicolour patterns on a figured ground of both dark and light Indigo.

Taken in the above order, these are produced according to the several directions given below.

Style 1.—On white cloth print Resist White II., Resist Yellow VIII., Resist Yellows III., IV., or VI., and a thickened solution of strong caustic soda.

Paste N.A.

900	grms.	caustic soda 75° Tw.
100	,,	British gum powder.
1000		

Mix together in the cold, and then heat gently until the paste is smooth.

After printing, hang, dip blue to the required depth of shade, wash well, sour, chrome, etc., as usual. The caustic soda mercerises the cloth locally, and consequently, wherever it is printed, a darker blue appears on dyeing, since mercerised cloth possesses a much greater affinity for Indigo than plain cloth. The dyeing of the ground shade ought to be commenced in very weak vats in order to allow the Paste N.A. to soften, and eventually dissolve off the cloth. In this way the stronger dye liquors that follow the first dipping are enabled to

penetrate into the fibre of the mercerised portions of the cloth and to dye it a full, even, deep blue, which contrasts well with the lighter shade they impart to the unprinted portions.

Style 2.—The production of a multicolour pattern which includes a light Indigo object on a dark Indigo ground calls for the employment of what are known as discharge resists. The light blue object or pattern is obtained by first dyeing the cloth a light blue, then printing an ordinary white resist upon it, and finally dipping it into the vat again until the ground shade is sufficiently dark. On now washing off the resist a blue pattern, instead of a white one, appears on a darker blue ground. If white, yellow, and orange are also required in the reserved pattern, it is obvious that their respective reserve pastes must not only be capable of resisting the dark blue ground, but also of actually discharging the light blue ground upon which they are necessarily printed. To this end, therefore, the ordinary resist pastes are modified by the addition of an *insoluble chromate.* During the souring operation, after the final dyeing, free chromic acid is liberated from this chromate and discharges the light blue, in the same way as the well-known Chromate Discharge already dealt with. (See discharges on Indigo.) Green and olive resists are simply obtained by the superposition of yellow and orange on light blue.

The chromates of lead, barium, and zinc are all suitable ingredients of discharge resists—the first two for yellow and (or) orange, the third either for white, yellow, or orange. The lead and barium chromates are unsuitable for white effects, because they deposit on the cloth insoluble sulphates, which afterwards become converted into chromates again during the chroming operation after the final dyeing ; zinc sulphate is soluble, and is removed from the fabric in process.

Discharge-Resists (for Indigo).

White D.R. :—

200	grms.	zinc chromate 65 per cent. paste.
800	,,	thickening D.R.
1000		

Yellow D.R. :—

40	grms.	Diamine fast yellow B.
100	,,	20 per cent. British gum paste.
100	,,	50 per cent. China clay paste.

Boil and add—

610	,,	thickening D.R.

Heat until the dyestuff is dissolved, and then add—

150	grms.	zinc chromate 65 per cent. paste.
1000		

Orange D.R. I. :—

350	grms.	water.
100	,,	flour. Boil, and add at 65° C.—
25	,,	copper sulphate (powder).
25	,,	copper acetate (powder).
100	,,	copper nitrate (100° Tw.).
250	,,	lead sulphate 50 per cent. paste.

Cool, and grind in—

150	,,	lead chromate 65 per cent. paste.
1000		

ORANGE D.R. II.:—	150	grms.	zinc chromate 65 per cent. paste.
	850	,,	white (or yellow) Resist III.
	1000		

THICKENING D.R.	550	grms.	water.
	170	,,	flour.
	30	,,	tallow. Boil, cool a little, and add—
	90	,,	copper sulphate.
	100	,,	copper acetate.
	60	,,	copper nitrate (100° Tw.).
	1000		Cool.

For the production of a multicolour pattern consisting of white, yellow, orange, and blue flowers, with green and olive leaves on a dark blue ground, the following colours are printed on *light* Indigo blue cloth:—

For White	print:—	White D.R.
,, Yellow	,,	Yellow D.R.
,, Orange	,,	Orange D.R. I. or D.R. II.
,, Blue	,,	White Resist II.
,, Green	,,	Resist Yellow VIII.
,, Olive	,,	Yellow Resist III., IV., or VI.

The blue, green, and olive colours simply resist the dyeing of the dark blue ground without affecting the lighter blue upon which they are printed; consequently, on washing off and chroming, they leave light blue, green, and olive on a blue ground, the green and olive being obtained by the superposition of yellow and orange on light blue.

After printing, the goods are well dried, dipped dark blue in the Indigo vat, washed in water, and then passed through a discharging or cutting bath consisting of—

60	parts	sulphuric acid 168° Tw.	at 50°–60° C.
25	,,	oxalic acid	
1000	,,	water	

After cutting, in which the light blue is discharged by the chromic acid liberated from the zinc or lead chromate, the goods are well washed, passed through a cold solution of lime water, and then chromed and oranged as already described; finally, they are well washed again and dried.

Style 3.—White, green, and yellow effects on a dark blue ground are produced according to the methods of Style 2 above.

Style 4.—This style is based upon the same principle as Style 1, but instead of the dark blue registering with the resist colours, it is arranged to fall over them in a haphazard fashion; indeed, it is really a cover pattern. Effects of white, yellow, orange, etc., on a two-blue ground are obtained by first printing the white cloth with ordinary resist colours, then, after drying, with the caustic soda paste already given under Style 1. On dyeing cloth so treated, the parts of the material to which caustic soda has been applied dye up darker than the rest of the ground, thus producing a two-tone effect. The reserved pattern runs through both shades of blue without any break in its continuity of line. The local contraction of the cloth due to mercerisation is got rid of in process—the numerous washings, sourings, etc., tending to straighten out and flatten any cockling that may appear before dyeing.

Another method of attaining the same result is to print the caustic soda first on white cloth; then wash well and dry on a stentering machine, which

effectually stretches the cloth out to its original width and frees it from all creases. The printing of the reserve pastes is then carried out in exactly the same manner as for ordinary cloth.

A process largely practised at one time, but now rarely used, depends upon the application of Manganese bronze. The cloth is first printed with a thickened solution of manganese sulphate or chloride. After drying, the bronze is developed in caustic soda and bleaching powder solution, well washed and dried. White and coloured resists are then blocked in on the unprinted parts of the cloth, and the dipping, washing, souring, and chroming proceeded with as usual. The parts of the cloth upon which the bronze is printed dye up a darker blue like mercerised cloth, but, unlike the latter, only the lighter blue can be reserved, for wherever the resists fall over the bronze, the result is a brown.

Resists under Indigo dyed with Indigosol O.—The principle involved in the production of resist effects under Indigo dyed by this process is exactly the reverse of that applied in the resisting of Indigo dyed by ordinary methods. In the first place, the cloth is padded with the dyestuff *before* the resists are printed ; in the second place, the resists themselves consist of *reducing* agents which, by preventing the oxidation of the Indigosol O., render impossible the fixation of Indigo upon the printed parts.

Of the several reducing agents suitable for the purpose, hydrosulphite-formaldehyde is undoubtedly the best, since it not only gives a perfect resist, but is also applicable to the widest range of effects.

The process is carried out as follows :—Pad the cloth in one or other of the solutions of Indigosol O. given below.

	Light Shade.	Dark Shade.
Indigosol O.	60 grms.	100 grms.
Glycerine	15 ,,	20 ,,
Turkey-red oil	15 ,,	20 ,,
Hot water	795 ,,	735 ,,
Nitrite of soda 98 per cent.	15 ,,	25 ,,
Cold water	100 ,,	100 ,,
	1000	1000

Dry, and print the following reserves or resists :—

White Resist.

150	grms.	hydrosulphite-formaldehyde.
250	,,	British gum.
400	,,	water. Heat to 160° F., cool, and add—
100	,,	zinc oxide.
100	,,	cold water.
1000		

Lake or Pigment Colour Resists.

400	grms.	Lake colour in paste.
250	,,	6 per cent. tragacanth thickening.
150	,,	hydrosulphite-formaldehyde.
200	,,	egg albumen solution 35 per cent.
1000		

Any lakes made from Basic colours which withstand hydrosulphite are suitable for these resist colours.

Basic Colour Resists.

10	grms.	Rhodamine 6 G.H. extra.
270	,,	water.
150	,,	resorcin.
150	,,	British gum (dry).

Dissolve, and add—

100	grms.	zinc oxide.
50	,,	water.
100	,,	formaldehyde 40 per cent.
150	,,	hydrosulphite-formaldehyde.

To 1000

Other suitable colours are Acridine orange D.H., Thionine blue G.O.O., Acridine yellow G., and Rhodamine B.—all used at 30 grms. per kilogramme of colour.

Vat Colour Resists.

300	grms.	Indanthrene yellow R. or G. paste.
40	,,	caustic soda 66° Tw.
40	,,	carbonate of potash.
40	,,	hydrosulphite of soda ($Na_2S_2O_4$).

Heat to 140° F. until the dyestuff is reduced, and then add—

60	grms.	dissolving salt B.
420	,,	starch-tragacanth thickening.
100	,,	Formosul.

1000

The padded cloth, printed with any of the foregoing resist colours, is dried and steamed for 2-4 minutes at 216° F.; it is then passed through the usual acid bath containing 20 grms. sulphuric acid 96 per cent. per litre. For lake-colour resists the bath is heated to 122° F.; for the other resist colours it is worked cold, and for Basic colours it contains only 10 grms. of acid per litre. When the ground shade is fully developed the goods are washed (and soaped for vat colours) and dried. Simple white resists do not require any steaming, being simply printed and passed into acid at once.

Azoic Colour Resists under Indigo.—By adding the diazo compounds of para- and meta-nitranilines, ortho-nitroparaphenetidine, etc., to Indigo resist pastes, very fast and bright red, orange, and pink effects are obtained.

The cloth to be treated is prepared in β-naphthol, and starched at the same time.

β-Naphthol Prepare.

15	grms.	starch.
429	,,	water.

Boil, cool to 60° C., and add—

30	grms.	β-naphthol.
120	,,	caustic soda 50° Tw.
300	,,	water.
6	,,	tartaric acid.
5	,,	tartar emetic.
80	,,	water.
15	,,	Turkey-red oil 40 per cent.

1000

Pad the cloth in the above, dry, and *cool.* Then print on any of the ordinary white resists together with the following:—

RED RESIST.

860	grms.	Resist paste (below).
120	,,	Diazo P.N.O.A. (below).
20	,,	sodium acetate.
1000		

DIAZO P.N.O.A.

135	grms.	*p*-nitro-*o*-anisidine.
275	,,	hydrochloric acid 36° Tw.
175	,,	hot water.

Cool after dissolving, and add—

375 grms. ice.

Then add slowly and with constant stirring—

58 grms. nitrite of soda (solid).

To 1000 c.c.

RESIST PASTE.

275	grms.	gum Senegal 50 per cent.
75	,,	water.
200	,,	lead nitrate.

Dissolve hot, and add—

300	grms.	lead sulphate 66 per cent. paste.
150	,,	zinc chloride (solid).
1000		

After printing, dry the goods gently, and when quite dry proceed to dip in the vat, etc., in the usual manner. Owing to the fact that copper salts cannot be used in conjunction with Azoic colours, and that lead salts cannot be kept in solution at a strength sufficient to resist the darkest blues, the insoluble Azoic colour resists are only applicable to the darker medium shades of Indigo.

In addition to those already described, there are other methods of obtaining resist effects under dyed Indigo blue. Strong solutions of tannic acid in combination with Basic colours have been used, but the results leave much to be desired. Lead peroxide (PbO_2), a powerful oxidising agent, has also been employed with success for white or yellow and orange resists: it is not, however, in general use, and, except perhaps for special styles, it offers no advantage over the older copper-lead-zinc resist pastes.

Goods printed with resist pastes may be dyed in either the continuous dyeing machine or by alternate immersion in, and exposure to the air above, the dipping vat (which see). The latter method, though more tedious, is usually preferred for the Indigo resist styles. In continuous dyeing machines, where the cloth passes over and under a great number of guide rollers, the resist pastes are very liable to crack, and to break off or be rubbed off the fabric. In dipping vats, on the contrary, the pastes remain quite undisturbed, the only danger being that they may slip if the dyeing is prolonged by the use of vats that are too weak. When this danger is apprehended, it may be avoided by dipping the goods at the outset in a vat containing an excess of

lime, or by raking up the vat in which the goods are dipped first. The number of dips required to produce a given shade depends mainly on the strength of the vats. The best vat for the purpose is the zinc lime vat; and in works where the resist style is produced in large quantities, the vats are usually worked in series of from three to eight. Each vat is exhausted in turn, so that no delay occurs during the setting of a fresh vat. A full dark blue can be dyed in four dips with the vats set and worked as below.

	1st.	*2nd.*	*3rd.*
Water	20,000 litres	20,000 litres	20,000 litres.
Zinc dust	7,200 grms.	10,800 grms.	20,250 grms.
Lime	16,000 ,,	24,000 ,,	45,000 ,,
Indigo pure	8,000 ,,	12,000 ,,	22,500 ,,

The cloth, stretched on the dipping frame, is immersed in the first vat for 15–20 minutes, then withdrawn and suspended over the vat for 10–15 minutes to drain and to allow the indigo-white to oxidise. The frame is then reversed and plunged into the second vat, where it remains for 10 minutes. The operations of withdrawal, draining, and oxidation are repeated, the frame again reversed, and immersed in the third vat for 10 minutes. The cloth is then exposed to the air for about 10 minutes, again reversed, and the operations repeated. After the final immersion the goods are exposed to the air for 20 minutes, and then washed, soured, chromed, and so on, according to requirements. The object of reversing the frame after each immersion is to ensure the level dyeing of the goods between selvedge and selvedge.

Reserves under other Vat Dyes.

Most of the resist pastes used for Indigo vats may also be employed for the modern Vat dyestuffs of the Ciba, Caledon, Indanthrene, Algole, and other groups, and therefore it is unnecessary to give special recipes for these products. Most of these Vat dyestuffs are applied by methods essentially similar to those employed for Indigo, the main difference being that many of them are best dyed at a fairly high temperature (40°–60° C.). In other respects the process is practically the same, with, of course, slight variations according to the nature of the particular dyestuff employed.

Vat colours of the Indigoid group lend themselves admirably to the production of reserve effects, and they may be dyed, like Indigo, either *continuously* or *by dipping*. In dyeing by the former method, the goods pass successively through two dye vats, with an exposure to the air between the immersions.

The first dye vat has a capacity of 1500 litres and the second 500 litres. Both are fitted with an arrangement of guide rollers and a pair of squeezing bowls at their exit ends. The formation of creases is best avoided by using conical opening rollers at the entrance of each vat, and also immediately in front of the squeezing bowls; the alignment of the guide rollers must also be perfect, any slight deviation from parallelism giving rise to creases and double edges, with their inevitable result—streaky dyeing. The exposure to air is effected by any of the systems in current use, but, taken altogether, the travelling band or creeper arrangement is the best, as the goods, after passing over a few rollers, are allowed to fall in regular pleats upon the moving band or apron. In this way the goods are plaited down gently in separate pleats instead of being piled up in a heterogeneous mass, to the almost certain damage of the resist paste.

For continuous dyeing with Vat dyestuffs, the best vat to use is the

hydrosulphite vat. An example illustrates the principle of preparing the dye liquors:—

Dye Vat for Continuous Dyeing (Ciba Colours).

I. { 30 parts any Ciba dyestuff in powder.
22·5 ,, caustic soda 66° Tw.

Mix into a paste and add—

II. { 500 parts cold water.
90 ,, hydrosulphite of soda in powder 85 per cent.
25·5 ,, caustic soda 66° Tw.

Dissolve cold. Mix I. and II. well together, and then pour over the whole—
1250 parts hot water.

Heat gently until the dyestuff is completely reduced to the leuco compound, and then make up to 10,000 parts by the addition of water to which a little hydrosulphite and caustic soda have been added to deprive it of its free oxygen.

Excess of either hydrosulphite or caustic soda is to be avoided, as both hinder the oxidation of the leuco compound on the fibre.

The two vats of the continuous dyeing machine are filled with liquor made up as above, the proportions being the same for both. The cloth, printed with suitable resists, is then passed through the first vat, aired for a few minutes, then passed through the second, aired again, and then rinsed in water. The goods are now soured in sulphuric acid (2 grms. H_2SO_4 168° Tw. per litre) at 35°–40° C., well washed, and then, if only a white resist has been printed, they are soaped at the boil for a few minutes to obtain bright and fast shades, and finally well washed in water and dried. In the case of lead yellow or orange resists the soaping must be omitted, since lead sulphate is soluble to some extent in slightly alkaline soap liquors. In place of soaping, therefore, the full development of the dyed ground, together with that of the lead yellows, is brought about by treating the goods for a few minutes at 70° C. in a chrome bath containing 25–30 grms. of bichromate of soda and 15–20 grms. acetic acid 9° Tw. per litre of water. They are then well washed and dried.

With such modifications in the composition of the resists and dye liquors as are demanded by circumstances, the same general methods are applicable to other Vat dyestuffs as are employed for the Ciba colours.

Reserves under Indanthrene Blue.—Although vat blues of the anthraquinone group, such as Indanthrene and Caledon blues, are satisfactorily reserved by the resist pastes in general use for Indigo, better results are obtained, in the case of coloured reserves, by means of more recent methods.

The Badische Company first suggested the use of manganese chloride and bichromate of soda, along with diazo solutions, for red reserves; but this process was not altogether successful in practice, and after undergoing several modifications, it was finally superseded by a mixture of zinc chloride, manganese chloride, and Ludigol (*m*-nitrobenzene sulphonate of soda), which gives excellent results if printed as a single colour or by the *last* roller in a multicolour pattern. Printed in any other place it is not sufficiently resistant to withstand the crush of the other rollers in the pattern and, consequently, gives an imperfect reserve.

A much simpler, and a very efficient, method of producing white and coloured reserves under Indanthrene blue, has been devised, and worked on the large scale, by J. Pokorny, who observed that manganese chloride *alone* was capable of preventing the fixation of Indanthrene blue in the dye bath. [1]

Red reserves are obtained by adding diazotised paranitro-orthoanisidine

[1] *Bulletin de la Société Industrielle de Mulhouse*, p. 257, 1920.

to the white reserve and printing on naphthol-prepared cloth; and, curiously enough, yellow reserves are obtained by an addition of Indanthrene yellow G. to the same white reserve. The yellow is fixed in the blue dye-bath.

A further interesting feature of Pokorny's process is that by adding a proportion of stannous chloride to the yellow reserve, it is possible to resist, simultaneously, both the red reserve and the blue ground, thus obtaining a clear-cut yellow pattern on a red and blue background.

The following methods of working may be taken as typical of the above processes:—

The cloth is bleached and, if red resists are to be printed, prepared in β-naphthol. It is then printed with the colours described below, dried, aired, steamed if necessary, and finally dyed in a continuous dyeing machine.

RESIST WHITE B.

75	grms.	China clay.
160	,,	British gum (powder).
240	,,	water.
300	,,	zinc chloride.
175	,,	manganese chloride.
50	,,	Ludigol.
1000		

RESIST RED B.

125	grms.	10 per cent. *p*-nitro-*o*-anisidine diazotised solution.
850	,,	white resist B. above.
25	,,	acetate of soda.
1000		

RESIST WHITE (POKORNY).

370	grms.	manganese chloride.
80	,,	water.
550	,,	starch-tragacanth thickening.
1000		

RESIST RED (POKORNY).

293	grms.	manganese chloride.
509	,,	starch-tragacanth thickening.
165	,,	paranitro-orthoanisidine 10 per cent. diazo solution.
33	,,	acetate of soda.
1000		

RESIST YELLOW (POKORNY).

240	grms.	manganese chloride.
200	,,	Indanthrene yellow G. paste.
60	,,	water.
500	,,	starch-tragacanth thickening.
1000		

This yellow is improved by a short ageing, but it fixes quite well in the dye bath without previous steaming.

For double reserves intended to resist both the ground and a red reserve :—

Double Reserves.	White.	Yellow.
Resist white (Pokorny)	1000	..
Resist yellow ,, ...	..	1000
Stannous chloride	150	150
	1150	1150

Print on cloth prepared in β-naphthol, dry, and over-print the red resist and dye.

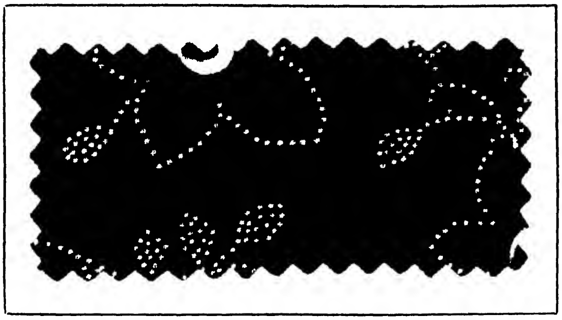
The dyeing of goods printed with the above colours demands great care to obtain successful results. It is preferably carried out in vessels made entirely of iron, furnished with iron rollers and squeezing bowls and heated by means of an iron steam coil. The capacity of the vessel should be about 200 gallons ; and the passage of the cloth through the dye liquor should be regulated to occupy 25–50 seconds according to the concentration of the dye bath and the depth of shade desired. The depth of shade, however, is dependent more upon the concentration of the dye bath than upon the duration of the passage. This last nevertheless exerts a certain influence on the result, and it is essential therefore to maintain both factors as nearly invariable as possible throughout the dyeing process.

The rollers in the dyeing tank are arranged to allow of 10 yards of cloth being always immersed in the dye liquor, and for most purposes a speed of 18–20 yards per minute is a sufficiently long passage. The goods are well squeezed on leaving the dye bath and are immediately run into a plentiful supply of cold water, followed by souring, washing, and soaping at the boil. The final wash and the soaping may be done either in the open width or in the rope form.

In order to comply with present-day demands for increased fastness, it is usual now to employ Naphthol A.S. combinations in place of those with β-naphthol for the production of resists under Indanthrene dyeings. In other respects the process remains unaltered.

The success of these styles depends largely upon the printing. The best results are obtained from block printing, either by hand or perrotine, since by this means much more colour is applied than when the printing is done from engraved copper rollers. Moreover, none of the colours in a multicolour pattern is crushed or smeared (*tech. : tailed off*) ; all remain on the surface of the cloth as more or less thick paste-like deposits and, in that condition, are at their best for acting as resists. If a roller printing machine must be used, it is advisable, indeed imperative, to print with as little pressure as possible on a soft blanket and soft lapping, and the rollers must be deeply engraved. Even then, and with more concentrated resists to help matters, it is not always possible to obtain results comparable with those obtained by block printing. With single-colour patterns little difficulty arises ; in multicolour patterns it is mainly the crush of following rollers that reduces the efficiency of the printed resists, and if this crush can be minimised, or compensated in other ways, it is quite possible to print satisfactory resists from engraved rollers. Machine-printed goods require to be very well dried before dyeing and then dyed as quickly as possible.

The two patterns illustrated have been block-printed ; a similar type of pattern, printed by machine, is shown in the section on "Resists under Sulphur Colours" ; it is dyed with a brominated Indigo over zinc chloride resists.



Indanthrene Blue R.S.N.3, resisted with Fast Red Salt 3 G.L. (I.G.).

The steps in the process are as follows:—

(1) NAPHTHOL PREPARE.

20 grms. Naphthol A.S. per litre.

(2) Print:—

WHITE RESIST.

Resist White B. (see p. 722).

RESIST RED.

70	grms.	Fast red salt 3 G.L.
120	,,	water.
100	,,	neutral starch-tragacanth paste.
160	,,	manganese chloride.
250	,,	zinc chloride.
270	,,	neutral starch-tragacanth paste.
30	,,	sodium acetate.
1000		

(3) Dry well and dye in:—

DYE BATH.

7·5	kilos.	Indanthrene blue R.S.N. 3 powder.
60	litres	glucose solution 1 : 1.
200	,,	water.

Paste well and pour into:—

500 litres water.

Heat to 170° F., and add:—

60–80 litres caustic soda 62° Tw.

3–4 kilos. sodium hydrosulphite ($Na_2S_2O_4$).

To 1000 litres in all.

Heat to 175°–185° F.

FEED LIQUOR:—

25	grms.	Indanthrene blue R.S.N. 3 powder.
122	c.c.	glucose solution 1 : 1.
500	,,	hot water.
80–125	grms.	caustic soda 62° Tw.
7–10	,,	sodium hydrosulphite.

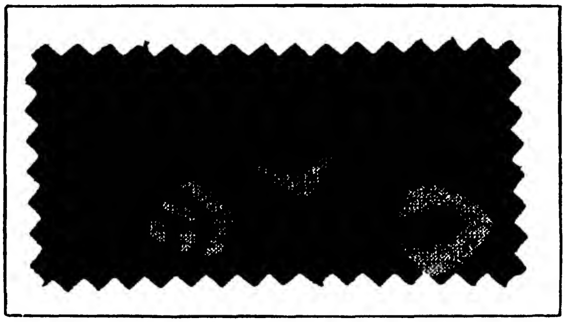
To 1000 c.c.

Use at 175°–185° F.—1 litre per kilogramme of cloth dyed.

The dyeing is carried out continuously in a small roller-vat of 200–220 gallons (900–1000 litres) capacity, furnished with squeezer bowls at its exit end. The dye bath is kept as nearly as possible at 175° F., and should not, in any case, be allowed to fall below this temperature. The speed of the goods through the vat should be adjusted to give a total immersion of 20 30 seconds, the rollers being arranged to allow of 10 yards of cloth always being in the dye liquor—in other words, a speed of about 20 yards per minute. On emerging from the dye bath the goods are squeezed so as to retain about 100 per cent. of their weight of dye liquor, then given a short air passage and immediately rinsed in a copious supply of cold water, soured in dilute sulphuric acid, rinsed again and finally soaped hot in the rope form with an addition of 2 grammes of sodium perborate per litre, washed and dried.

During the dyeing process the dye bath diminishes in strength and volume and requires to be replenished from time to time as the cloth runs through. With 100 per cent. expression, 1 kilogramme of cloth takes up 1000 c.c. of dye liquor; consequently, for every 10 kilos. of cloth dyed, 10 litres of the above feed liquor must be added to the dye bath in order to maintain the concentration and volume. The feed liquor is best added in a continuous manner from a supply vessel placed on a higher level and regulated to deliver at the rate of 1000 c.c. per kilogramme of cloth dyed.

Other Vat dyestuffs and Naphthol A.S. colours are applied in an analogous manner and permit of numberless combinations, none of which approaches the importance of the blue and, in a less degree, the green grounds, however. Apart from white, orange, and red resist colours on blue and green grounds, only the exceedingly fast brown from Naphthol A.S./Fast Scarlet salt G.G. is of practical interest.



Indanthrene Brilliant Green B., resisted with Naphthol A.S. colours (I.G.).

Naphthol Prepare.

Naphthol A.S. (20 grms. per litre).

Black Print.

60	grms.	Fast blue salt B. (Dianisidine).
400	,,	water.
500	,,	neutral starch-tragacanth paste.
40	,,	acetic acid 9° Tw.
1000		

Red Resist.

200	grms.	Diazo K.B. (overleaf).
100	,,	starch-tragacanth paste.
260	,,	starch-tragacanth paste.
160	,,	manganese chloride.
250	,,	zinc chloride.
30	,,	sodium acetate.
1000		

Diazo K.B.

10	grms.	Fast red K.B. base.
150	c.c.	water.
10	,,	hydrochloric acid 32° Tw.

Cool, and add—

10	grms.	ice.
4	,,	sodium nitrite.
To 200	c.c.	

Orange Resist.

70	grms.	Fast orange salt G.C.
130	,,	water.
100	,,	starch-tragacanth paste.
160	,,	manganese chloride.
250	,,	zinc chloride.
260	,,	starch-tragacanth paste.
30	,,	sodium acetate.
1000		

Print, dry well, and dye in :—

Dye Bath.

20	kilos.	Indanthrene brilliant green B. double paste, fine.
200	litres	hot water.

Mix well and add to—

500 litres hot water in the dye vat.

Heat to about 150° F., and add—

100	litres	caustic soda 62° Tw.
6	kilos.	sodium hydrosulphite conc. ($Na_2S_2O_4$).
15	,,	Dekol.

per 1000 litres.

Dye at 160° F.

Feed Liquor.

45	grms.	Indanthrene brilliant green B. double paste, fine.
500	c.c.	hot water.
230	,,	caustic soda 62° Tw.
10	grms.	sodium hydrosulphite.
20	,,	Dekol.
1000	c.c.	

Dye at a regular temperature of 160° F. and complete the process in exactly the same manner as described for Indanthrene blue dyeings.

The production of a bright Azoic yellow resist in combination with red or orange, etc., resists is not possible owing to the fact that the yellow-yielding naphthols give nothing but yellows or browns with all Fast colour bases. If, therefore, a mixed colouring containing yellow is required, recourse must be had to the Indigosol yellows, which, in common with several other Indigosols, are well adapted to fill in the gaps in the range of Azoic colour resists under Indanthrene dyeings.

Indigosol Resists under Indanthrene Dyeings.—Two processes are available for this purpose, viz. (*a*) the Copper-Lead Salt Process, and (*b*) the

Ludigol-Manganese Process. Both may be applied to naphtholated or unnaphtholated cloth according to circumstances.

Naphtholated cloth is used when the Indigosol resists are associated with ordinary Azoic colour resists as already described; unnaphtholated cloth is used when the Indigosols are printed alone or along with a Rapid fast colour resist. The latter combination is not often employed, brighter red and orange resists being obtained by printing the diazotised bases on Naphthol A.S. prepares.

Although the Indigosol resists permit of a fairly complete range of coloured effects being obtained under Vat colour dyeings, they are mainly important for the production of yellows and greens, which, along with orange and red resists, cannot be got from Azoic dyestuffs. In practice they are regarded rather as supplementary to the Azoic colour resists than as forming the basis of a separate style, and it is as supplementary colours that they find their chief employment in the class of work under discussion. The Indigosols are, however, capable of yielding a variety of fast resists under Vat colour dyeings, and it may be that, in the future, their use for this purpose will be extended, though it is not likely that Indigosol resists under dyed Vat colour grounds will ever replace the more reliable and convenient Vat colour resists under Indigosol padded grounds.

As Indigosol resists under Indanthrenes are not produced in this country, the particulars of the processes to be described have been selected from data supplied by the firms of Durand & Huguenin S.A. of Bâle and the I. G. Farbenindustrie A.G. of Frankfurt.

(a) *Copper-Lead Salt Process.*—The goods are printed with:—

	1.	2.	3.	4.	5.	6.	7.	8.	9.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol Yellow H.C.G.	50	..	..	..	..	..	..	..	..
,, Golden Yellow I.G.K.	..	60	..	..	..	..	..	..	..
,, Orange H.R.	..	..	60	..	..	..	..	..	..
,, Scarlet H.B.	..	..	..	60	..	..	..	..	..
,, Pink I.R. Extra	..	..	..	..	60	..	..	..	..
,, Red H.R.	..	..	..	..	..	75	..	..	..
,, Red Violet I.R.H.	..	..	..	..	..	..	75	..	..
,, Green A.B.	..	..	..	..	..	..	..	60	..
,, Printing Black I.B.	..	..	..	..	..	..	..	..	25
Water	100	60	70	60	60	75	75	80	115
Indigosol Developer G.A.	30	70	60	70	70	50	50	50	20
Glyceine A.	..	..	..	..	..	..	30	..	..
Rongalite C.	..	20	..	..	..	..	..	..	..
Reserve A.	820	790	810	770	770	760	730	810	840
Indigosol Developer D.	..	..	..	20	20	20	20	..	..
Sodium chlorate 50 per cent.	..	..	..	20	20	20	20	..	..
	1000 grms.								

RED.

150	grms.	Rapid fast red 3 G.L.
30	,,	Turkey-red oil.
50	,,	potassium chromate (K_2CrO_4).
550	,,	Reserve B. (overleaf).
220	,,	gum Senegal 1 : 1.
1000		

Reserves (A.) and (B.) [(C.) alternative to (A)].

	A.	B.	C.
	grms.	grms.	grms.
Copper sulphate	100	..	52
Lead nitrate	160	..	84
Copper acetate	120	..	63
Lead sulphate 60 per cent. paste	60	150	30
China clay 1 : 1	100	..	475
Gum Senegal 1 : 1	660	425	280
Ludigol	..	50	..
Zinc oxide	..	25	..
British gum 1 : 1	..	350	..
Water	..	..	16
	1200	1000	1000

Reserve (C.) is employed for block work.

After printing on unprepared cloth the goods are steamed for 10 minutes in fairly moist steam and then dyed, as already described, with Indanthrene blue, etc. After dyeing, the goods, if they contain a Rapid fast red, are passed through a strongly acid bath, followed by the usual washing and soaping.

If printed on naphtholated cloth, along with Azoic colour resists, the Indigosols are steamed as above and the goods then dyed and after-treated according to the ordinary procedure for Azoic resist styles.

(b) *Ludigol-Manganese Resist Process.*—This process is based upon the use of the manganese salt of *m*-nitrobenzene sulphonic acid as a resisting agent in place of Ludigol itself, which is the sodium salt of the same acid. Owing to their slight solubility in the hot alkaline dye bath, the heavy metal salts of Ludigol have little tendency to bleed and, consequently, when employed as resists they give sharper impressions of the pattern than do more soluble materials. The Ludigol-Manganese compound is prepared by precipitating Ludigol with manganese chloride and, being an acid oxidising agent, it plays the double rôle of resist for dyed Indanthrenes and of developer for the Indigosols with which it is mixed for coloured resists.

The printing colours are prepared according to the usual methods for Indigosols ; they work well and are quite stable.

Printing Colours.

	1.	2.	3.	4.	5.	6.	7.	
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	
Indigosol Orange H.R.	60	..	..	..	..	..	..	
„ Golden Yellow I.G.K.	..	50	..	..	..	..	..	
„ Red H.R.	..	..	60	..	..	..	..	
„ Pink I.R. Extra	..	..	..	30	..	..	..	
„ Green A.B.	..	..	..	..	80	..	..	
„ Printing Black I.B.	..	..	..	..	..	20	..	(fór grey)
„ Red Violet I.R.H.	..	..	..	..	..	..	40	
Glyecine A or Fibrit D.	20	30	..	50	..	..	80	
Solution Salt B.	20	..	..	50	..	..	..	
Indigosol Developer D.	..	30	..	..	40	..	..	
„ „ G.A.	..	..	..	..	50	..	..	
Water	100	135	175	110	100	100	120	
Natural gum 1 : 1	540	510	550	500	520	620	520	
Sodium chlorate 1 : 3	30	25	35	60	30	90	50	
Ammonium vanadate 1 per cent.	10	20	10	20	30	10	10	
Ludigol-Manganese paste 65–70 per cent.	200	200	150	150	150	150	150	
Ammonium lactate	20	..	20	30	..	10	30	
	1000 grms.							

LUDIGOL-MANGANESE PASTE.

$\begin{cases} \text{200 grms. Ludigol.} \\ \text{300 c.c. hot water.} \end{cases}$

Dissolve hot and add slowly—

$\begin{cases} \text{220 grms. manganese chloride.} \\ \text{250 c.c. hot water.} \end{cases}$

Allow to stand until cold, when the manganese compound settles out in the form of fine, yellowish crystals. Filter off the crystals and press them until the mass weighs about 375 grammes, which corresponds to a paste of 65–70 per cent.

The lactate of ammonia in the foregoing recipes is merely commercial lactic acid neutralised with ammonia until a slightly alkaline reaction is obtained.

After printing, the goods are dried well and steamed for 5–10 minutes in the rapid ager ; they are then allowed to lie overnight and subsequently dyed with Indanthrene blue, etc., in the roller vat as usual for resist styles, *e.g.* a passage of 20–30 seconds through the dye bath, followed by squeezing, washing, souring, washing, and soaping at the boil. It is advantageous to add 1–2 grms. of potassium sulphocyanide per litre of souring bath.

CARE OF INDANTHRENE DYE BATHS. From the description of the dyeing process it is evident that the dye baths are not exhausted ; in fact, if the dyeing and replenishing have been conducted properly, a dye bath of 200 gallons will still retain about 90 per cent. of its original strength, so far as dyestuff is concerned, and about 80 per cent. of its alkalinity. A portion of the dyestuff, too, will probably be re-oxidised. To bring it up to standard for a fresh dyeing it is, therefore, only necessary to add 10 per cent. of the original amount of dyestuff and 20 per cent. of the other ingredients.

During the course of long-continued working dye baths become overcharged with the decomposition products of caustic soda, naphthol, and hydrosulphite, and require periodical purification. For this purpose they are cooled down and well stirred up, a little acid being added to bring about the precipitation of the colouring matter. After settling for some time, the supernatant brown liquor, containing the impurities, is drawn off, and the pasty mass of dyestuff, remaining at the bottom, is washed once by decantation, and then strengthened, as mentioned above, by the addition of 10 per cent. of its original weight. The amounts of glucose, caustic soda, and hydrosulphite added are, naturally, the same as those used in setting the vats in the first instance.

The brightness of all Indanthrene and Caledon blue dyeings is considerably enhanced by steaming for half an hour in moist steam after the final wash.

Several other dyestuffs of the anthraquinone series lend themselves equally well to the production of reserve effects by the above process—notably the Caledon blues, olives, greens, and browns—but, with the exception of the brighter brands of the blues, they are of extremely limited application.

Batticks.

A peculiar kind of resist work, known as "Battick printing," has been practised since very early times in the East, and more especially in Java. The production of the native article depends upon the application to the cloth of purely mechanical resists composed of wax, resin, and fatty matters. These substances are applied in the melted state by pouring them from small vessels of calabash gourd or metal, through which openings of various sizes have been pierced ; sometimes the openings are fitted with a small wooden spout, but

usually the spout itself is the pointed part of the gourd to which the stem is attached. The worker pours the melted wax over those portions of the cloth which are required to remain uncoloured; and when the resist has set and hardened, the goods are dyed by dipping in an Indigo vat, or in a cold bath of other vegetable dyestuff or a mordant. The resist is afterwards removed by treating the dyed material in boiling water, to which is sometimes added soda or potash (wood ashes) so as to form an easily removable emulsion. For a repeating pattern brass blocks are used in Java.

The characteristic feature of typical Battícks is the appearance of fine veins of colour running irregularly across the reserved parts of the pattern. Sometimes a fine network of two or three different colours extends over every white (or rather buff) object in the design, giving to the whole an extremely rich and beautiful quality. This artistic appearance is due to the cracking of the rather brittle waxy resists during the handling of the cloth in the dyeing process; and the more brittle and the thicker the protecting layer of wax, the more likely is it to crack. In dyeing, the dye liquor penetrates through the interstices of the resist and becomes fixed on the cloth so exposed, thus causing the curious marble-like veinings alluded to above.

Imitations, more or less successful, of the Battick style are obtained in Europe by printing melted wax from engraved rollers or plates, also by stencils; and many beautiful effects are produced by first dyeing in one colour, then breaking the resist and re-dyeing in another colour. If necessary, the resists can be applied afresh as often as desired, thus affording a means of obtaining a great variety of colour effects, both directly and by superposition.

The Battick style may be, and is, also applied in Madder dyeing, as well as to the Vat colours. In such cases the cloth is mordanted after the resist has been printed, dried, and broken into cracks (by passing over a small roller). For example, a red, blue, chocolate, and buff effect is obtained in the following way:—(1) Print on melted beeswax, allow to set hard, and then pass the goods over a roller (to break up the layer of wax) into a cold solution of acetate of alumina 8° Tw., hydro-extract the excess of liquor, and hang the goods in a cool room until dry. Then raise the temperature to 30°–40° C. for the purpose of ageing the goods, taking care not actually to melt the resist, and then dung in the ordinary way; wash the goods in boiling water for 15 minutes; wash again in borax solution at the boil, and when the wax is quite dissolved off the cloth give a final wash in hot water, and proceed to dye with Alizarin exactly as for Madder reds. (2) Clear and brighten the red as usual, dry the cloth, and print any desired pattern upon it in melted wax. (3) Break the wax resist again and dip in the Indigo or any other blue vat; wash, sour lightly; wash in cold water; wash in borax or soda-ash solution at 75°–80° C. to remove the last traces of wax, and then dry up. The ultimate effect will consist of red and white (where the second resist was printed), blue and chocolate, the last by the superposition of blue on red, and over the whole pattern various veins of red, blue, and chocolate will appear. The buff colour, in place of white, is obtained by finally tinting the cloth in the padding machine with a suitable Direct dyestuff such as Chrysamine. Similar, but less permanent, effects can be obtained from Basic dyestuffs on a tannin mordant, and, in short, the process is suitable for any colouring matter or mordant which can be applied at a temperature low enough to prevent the melting of the resist.

Resin is largely used in place of wax for battick printing by machine; it is cheaper, gives almost identical results, and lends itself to a greater variety of styles. Its only preparation for printing consists in previously melting it at a temperature sufficient to render it fluid. In this state it is best printed by heated copper rollers, preferably those furnished with an internal electrical

heater, such as that patented by F. Ashton and the Calico Printers' Association, Ltd. The colour box may also be heated if necessary. In other respects the resin process follows on the lines of the wax process and may be adapted to the same ends.

An interesting property of resin was observed by F. Ashton and G. Nelson during the course of experiments on its application to the resisting of metallic mordants.[1] When resin-printed cloth was slop-padded in chromium mordants containing hydrosulphite-formaldehydes, it was found, contrary to expectation, that the resin, instead of resisting the mordants, combined with them and fixed a much larger amount of chromium on the printed parts of the cloth than was fixed on the unprinted parts. The resinate of chromium thus formed resists the treatment necessary for the removal of the excess of resin and, consequently, on dyeing up in Alizarin, etc., a dark pattern is obtained on a lighter ground of the same shade. The best chromium mordant for the purpose was found to be a mixture of bichromate of soda and Formosul or other similar product. Analogous results are obtained with other metallic mordants such as salts of iron, aluminium, nickel, etc.

Simply applied, as above, the process yields effects in gradations of one colour only. If, however, the resin-printed cloth be dyed Indigo before being mordanted the results are quite different. The resin resists the Indigo and fixes the mordant, and, on being finally dyed up in mordant colours, an entirely new battick style is produced, viz. a cracked pattern in colour (not white as usual) with blue veins running through it, on a dark Indigo blue ground. The shade of the ground is, of course, modified somewhat by the superposed mordant colour, but this only serves to increase the variety of colour combinations obtainable from the process.

Further modifications are possible, and a vast number of combinations are realisable by employing combined processes and different mordants. Azoic colours, resists, and discharges may be printed on the resin-printed cloth either before or after dipping in Indigo ; or before, after, or along with the resin, afterwards dyeing in Indigo, followed always by a subsequent dyeing in mordant colours. By these and other means an almost illimitable variety is possible ; and when it is considered that any of the members of the Vat and Mordant colour series may be utilised, it will be readily understood that the resin process of battick printing yields effects too numerous to describe in detail.

Resists under Printed Indigo.

White resists under printed Indigo are obtained by printing certain acid metallic salts, flowers of sulphur, lactic acid or ammonium nitrate under the ordinary printing pastes used for Indigo styles. For the glucose process sulphur is, by far, the best resist.

Resist S.

150	grms.	flowers of sulphur.
50	,,	lactic acid 50 per cent. (optional).
800	,,	30 per cent. gum Senegal solution.
1000		Grind several days until a perfectly smooth paste is obtained.

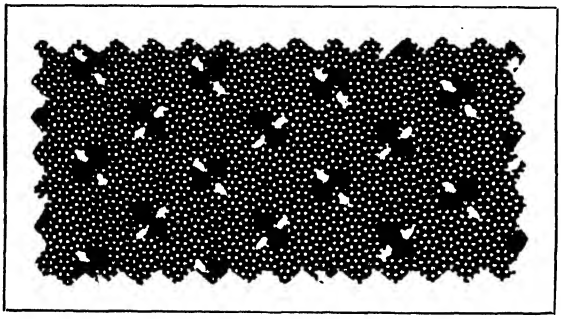
Print on glucose-prepared cloth, dry, and cover with a thickened mixture of Indigo and caustic soda, steam, wash, etc., exactly as described under the

[1] English Patent No. 159552, 1919.

printing of Indigo. The same resist is also suitable under the hydrosulphite Indigo printing pastes; and for heavy resist patterns, the lead-copper resists may often be employed successfully.

Fast-coloured resists are obtained by mixing diazo solutions with sulphate of alumina and lactic acid pastes, and printing on cloth prepared with β-naphthol. After applying the resist paste, the Indigo is printed over it and steamed, etc., as usual.

Success in the printing of sulphur resists depends entirely upon (1) the quality of the sulphur employed, (2) the percentage proportion used in the printing paste, and (3) the consistency of the printing paste. A sample of the sulphur ought to be completely soluble in carbon bisulphide, and quite free from grit of any description—in short, the finest quality of precipitated sulphur. As regards the quantity used, 120 grms. per litre of printing colour is usually sufficient for most purposes. At this strength the finest patterns resist a dark Indigo cover. Occasionally it is necessary to use a stronger resist (140–160 grms.) for heavy cover patterns; but, unlike most resists, an increase in the strength of a sulphur resist beyond a certain point is more likely to defeat than to achieve the object in view, because it sticks in the engraving, filling it up, and thus causes less sulphur to be transferred to the cloth than would have been the case had a weaker resist been used in the first instance. Either a gum Senegal, or a British gum thickening, is best suited for carrying sulphur, and its consistency must be such as to prevent the sulphur from settling quickly, and yet not too thick to print properly. Some settling always occurs, and for this reason sulphur resists are always stirred up by the printer every time he feeds his box.



Sulphur resist under printed Indigo.
(C.P.A.).

Reserve Salts W. and O.—Under these names two organic bodies were placed on the market, by Kalle & Co., as substitutes for sulphur in resists under printed Thio-indigo colours and Indigo. In some respects they behave similarly to the Leucotropes (the Salt W. giving a white, and the Salt O. a yellow resist), and they possess an advantage over sulphur in that they are free from the defect of causing an etching action on the roller immediately following them. At the same time they do not produce a good resist if they are crushed by following rollers, and consequently they must be worked last—a condition which limits their use for Indigo work, because, in such work, it is imperative to print the Indigo last in order to obtain the full richness and bloom of the blue. For single colour resists under Indigo, however, they work well and as they give crisp impressions, they are sometimes preferred for this style.

Resist White R.S.

200	grms.	Reserve salt W.
800	,,	British gum thickening.
1000		

Resist Yellow R.S.

200	grms.	Reserve salt O.
800	,,	British gum thickening.
1000		

For light Indigo covers reduce above as required.

Print on glucose-prepared cloth ; cover Indigo and steam, chrome and wash, etc., as usual for Indigo.

Reserve salt W. is often combined with sulphur in order to improve the working quality of the resist. In this case it may be printed before the dark blue with satisfactory results.

Resists under Indigo printed by the Indigosol O. Process.—This style is illustrated and described in the section dealing with the direct printing of Indigosols. (See " Indigosols.")

Leucotrope Resists under Vat and Sulphur Colours.

Although zinc chloride is an effective resisting agent under many Vat and Sulphur dyestuffs, its hygroscopicity presents certain disadvantages in practice, and its substitution by the Leucotropes is, therefore, of interest to calico printers.

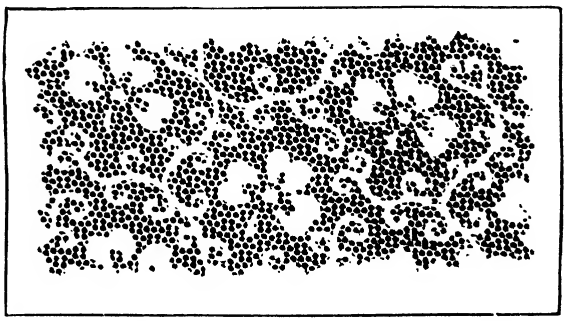
The Society of Chemical Industry in Bâle were the first to notice that Leucotrope printing pastes, containing *no* hydrosulphite-formaldehyde, were capable of preventing the fixation of Vat dyestuffs afterwards printed over them ; but they failed, at the same time, to observe that the presence of strong caustic alkalies was equally unnecessary, and, consequently, their process is of much less practical value than that of E. Bentz and the Calico Printers' Association,[1] in which caustic alkalies are absent altogether.

This latter process consists essentially of printing one of the Leucotropes, suitably thickened, on white cloth, and then over-printing suitable Vat colours (made up in the customary manner) with either a pad or cover roller. The Vat colours are fixed in the usual way by a run through the rapid ager, followed by a treatment in bichromate of soda or perborate of soda.

Example :—

150	grms.	Leucotrope O.
850	,,	British gum thickening.
1000		

Print, dry, and cover with a Vat or Sulphur dyestuff, dry, and run through a rapid ager, etc.



Leucotrope resist under Ciba Blue 2 B. (S.C.I.B.).

Almost all the Vat dyestuffs, whether derivatives of anthraquinone, Indigo, or Thio-indigo, are suitable for printing in cover-patterns, or plain pads, over a Leucotrope resist ; and similarly most members of the many groups of Sulphur colours, and the Hydron blues, are equally applicable. None of the Sulphur blacks, however, can be satisfactorily resisted by Leucotropes.

[1] English Patent No. 16389, 1910.

Another advantage of the process is that coloured resists may be obtained by adding a sufficiency of Leucotrope to colours, such as Alizarin red, α-Naphthylamine claret, and certain other colours, and then printing suitable Vat colours over them as above.

In the same way Leucotrope may be associated with mordants, and the goods, after covering, may be dunged and dyed up in any suitable mordant dyestuff.

Reserve salts O. and W. behave similarly. Under some Vat and Sulphur colours they give a perfect resist, but they are not so generally applicable as the Leucotropes.

The same remarks apply also to Ludigol, an organic oxidising agent which finds a limited application as a reserve for reduction discharge cover prints and as a resist under a few Indanthrenes.

Resists under Steam Alizarin Reds and Pinks, etc.

The development and fixation on the cloth of steam Alizarin reds, pinks, and light purples is prevented in presence of citrates, tartrates, oxalate of antimony, and citric and tartaric acids. The resists are usually printed on cloth prepared with Turkey-red oil, and then covered or padded on the machine with the Alizarin colours.

The following are a few of the more typical resists in common use :—

RESIST S.A. I. (for Pinks).	220	grms.	British gum.
	445	,,	water.
	200	,,	China clay paste 50 per cent.
	130	,,	citrate of soda 55° Tw.
	5	,,	citric acid.
	1000		Boil and cool.

RESIST S.A. II. (Pinks).	850	grms.	50 per cent. gum Senegal.
	150	,,	oxalate of antimony.
	1000		Boil and cool.

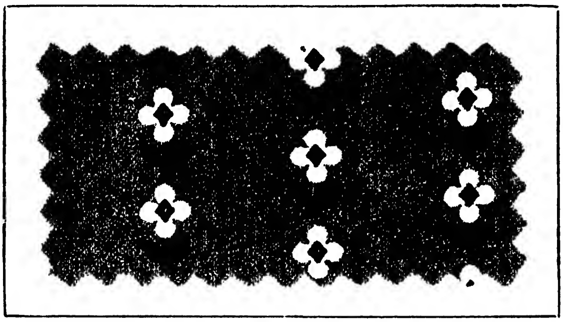
RESIST S.A. III. (Pinks).	200	grms.	China clay.
	100	,,	citrate of soda 55° Tw.
	100	,,	citrate of chrome 42° Tw.
	100	,,	water.
	500	,,	British gum paste.
	1000		

RESIST B.N. (strong Reds).	330	grms.	citrate of chrome 48° Tw.
	5	,,	citric acid.
	75	,,	China clay.
	90	,,	British gum.
	500		Boil and cool.

RESIST B.N.S. (Reds and Aliz. Bordeaux).	330	grms.	citrate of chrome 48° Tw.
	330	,,	citrate of soda 55° Tw.
	150	,,	China clay.
	180	,,	British gum powder.
	10	,,	tartaric acid.
	1000		Boil and cool.

The last two resists are excellent for white reserves under deep Alizarin reds and colours obtained from Alizarin bordeaux or grenat and aluminium mordants. When reduced with six times their weight of gum or paste, they give good whites under light Alizarin pink pads and covers. For deep pinks less reducing paste must be taken.

Print the above resists on cloth prepared in Turkey-red oil (2½–5 per cent. fatty acid); dry, and over-print in steam Alizarin red, pink, or bordeaux as the case may be; steam for 1 hour in the continuous steamer, and then wash well, soap, and dry. After steaming, the pattern printed in the resists has a decided yellow appearance, due to the presence of uncombined Alizarin,



Citrate of Chrome resist under Alizarin Pink.

but on washing and soaping, the Alizarin and the soluble aluminium and tin compounds are removed entirely from the fibre, leaving it perfectly pure and white.

Coloured resist effects under steam Alizarin pink pads are obtained by adding citric acid to the ordinary steam Basic colour pastes. This style was largely practised some years ago for the Eastern markets, and is still produced in notable quantities, although it has lost somewhat in popularity as a standard style.

COLOURED RESISTS UNDER STEAM ALIZARIN PINK.

	YELLOW S.A.	BLUE S.A.	GREEN S.A.
China clay	70	70	70
Water	60	60	60
British gum paste	620	620	619
Thioflavine T.	20	..	14
New methylene blue N.	..	20	7
Citric acid	10–15	10–15	10–15
Acetic acid 9° Tw.	100–95	100–95	100–95
Boil, cool, and add—			
Tannin 50 per cent. solution in acetic acid	120	120	120
	1000	1000	1000

Print on oiled cloth, dry, and cover or pad with a steam Alizarin pink containing 8 grms. Alizarin (20 per cent. paste) per kilogramme of printing colour; steam one hour without pressure, and then pass the goods through a solution of tartar emetic to fix the Basic colours; wash well, soap at the open width, wash again, and dry. The above recipes will serve for all Basic colours.

If a stronger pink ground is padded (on the printing machine), the proportion of citric acid must be increased accordingly.

White resists, and any steam colours deeper than the pink ground—*e.g.* Alizarin red, chocolate, Logwood black, etc.—are printed in combination with blue, yellow, and green resists when a greater variety of colour is required.

Another method of obtaining resist effects under steam Alizarin colours is based upon the employment of direct dyeing colouring matters with disodium phosphate as the resisting agent. This method does not yield very bright colours, nor is it of any great practical value, but it possesses a certain amount of interest, and may perhaps be of service in an emergency.

PHOSPHATE RESISTS UNDER STEAM ALIZARIN PINKS.

YELLOW :—
30 grms. Chrysophenine G.
30 ,, starch.
500 ,, 6 per cent. tragacanth thickening.
200 ,, water.

Boil, cool, and add—
50 grms. disodium phosphate crystals.
190 ,, water.

1000

BLUE :— as Yellow but 30 grms. Chicago blue 6 B.
GREEN :— ,, 20 ,, Thioflavine S.
10 ,, Chicago blue.
OLIVE :— ,, 19 ,, Chrysophenine G.
10 ,, Chicago blue O.G.
1 ,, Benzo fast scarlet 4 B.S.

Print on oiled cloth, dry, and print Alizarin pink with a pad roller ; steam one hour, wash, and soap. Tungstate of soda has been suggested for the same purpose by A. Scheurer, and gives excellent results.

Coloured resists by any process are not successful under strong Alizarin reds, nor are they suitable under steam Alizarin violets (iron), on account of the formation of blue tannate of iron or of yellow ferric phosphate. Hence white resists alone are of any importance under Alizarin reds, bordeaux, or violets.

Resists under Albumen Colours.

Insoluble pigment colours, fixed in steaming by the coagulation of albumen, can be easily resisted by means of any substance capable of bringing about the coagulation before the albumen comes in contact with the actual fibres of the cloth. For this purpose zinc sulphate, citric or tartaric acid, and ammonium nitrate have been found by experience to give the best results. They are used either alone or in combination with one another and China clay. The organic acids by themselves are only suitable for pale Ultramarine blues, and with these they produce very good white resists. The cloth is first printed with the resist pastes, then dried and over-printed with a cover or pad roller in the albumen colour ; it is then steamed one hour, washed, and soaped.

PIGMENT RESIST WHITE I.
240 grms. nitrate of ammonia (cryst.).
110 ,, China clay.
470 ,, water.
180 ,, dark British gum.

1000

Boil and cool.

WHITE RESIST P. II.

300	grms.	zinc sulphate (cryst.).
200	,,	China clay.
200	,,	citrate of ammonia 38° Tw.
150	,,	water.
150	,,	British gum.
1000		

Boil and cool.

Any of the citric acid resists used under steam pinks may be utilised for resisting light shades of Ultramarine blue.

Print the above resists on white cloth, dry, and cover in any of the Pigment printing colours given under the Steam Style ; steam one hour, wash, and soap.

Coloured resists are rarely produced under Pigment colour covers and pads. When required, they are best obtained by adding ammonium nitrate to the ordinary steam printing pastes, such as Alizarin red or pink. With Mordant colours which form fast zinc lakes, like Alizarin blue, the requisite amount of zinc sulphate to resist the Pigment colour acts also as a mordant for the blue, and no ammonium nitrate is required.

Resists under Basic Colours (Tannin).

Although antimony salts are the fixing agents *par excellence* for Basic colours printed in combination with tannic acid, they are nevertheless, when used in excess, very efficient, and in fact the best resisting agents for those colours. The particular salts used are sodium tartar emetic and oxalate of antimony, together with zinc sulphate and citric acid, respectively. The white cloth is printed with the resisting paste ; then dried, and over-printed with any of the Basic printing colours given in the section on the Steam Style ; steamed one hour, passed through a 1 per cent. solution of tartar emetic and washed, soaped, and dried.

If the antimony resist pastes contain, in addition to the usual ingredients, a little stannous chloride, they will serve as discharges for any suitable Direct dyestuff with which the cloth may have been previously dyed ; and if the Basic colour cover also contains a corresponding quantity of stannous chloride, it too will discharge the dyed ground, and an effect of a white pattern on a coloured discharged ground will be obtained.

WHITE RESIST B.T. I.

200	grms.	China clay.
250	,,	water.
150	,,	British gum.
200	,,	sodium tartar emetic..
180	,,	zinc sulphate.
20	,,	citric acid.
1000		Boil and cool.

RESIST B.T. II.

550	grms.	water.
100	,,	China clay.
175	,,	British gum.
150	,,	oxalate of antimony.
25	,,	citric acid.
1000		Boil and cool.

Resist B.T. III.

200	grms.	China clay.
275	,,	water.
125	,,	British gum.
400	,,	sodium tartar emetic.
1000		Boil and cool.

Print any of the above on white cloth; dry, and print any Basic colours containing tannin; steam for one hour, fix, wash, and soap.

For obtaining a white discharge on a Direct colour ground with simultaneous resist of Basic colour cover, print the following instead of the above:—

Resist Discharge Z.

50	grms.	China clay.
300	,,	water.
200	,,	British gum.
350	,,	sodium tartar emetic.
50	,,	citric acid.

Boil, cool, and add—

50	grms.	stannous chloride.
1000		

Print on cloth dyed with 1–2 per cent. Erika pink; dry and print a Basic green containing tannin and stannous chloride (5 per cent.); steam one hour, pass through a 1 per cent. solution of tartar emetic, wash, and soap. The ultimate result is a white pattern on a pink and green ground.

Multiple Resists under Steam Colours.

It is often required in practice to produce a white pattern on a multicolour ground (say, a three-colour stripe or check), consisting of two or more quite distinct classes of steam colours.

The following white resist paste will act efficiently under Alizarin red and pink, Basic colours and Pigment colours, so that it affords a means of producing the effect alluded to above:—

Triple Resist—Resist T.R.

200	grms.	sodium tartar emetic.
100	,,	China clay.
150	,,	zinc sulphate.
200	,,	citrate of chrome 46° Tw.
250	,,	water.
100	,,	British gum.
1000		Boil and cool.

Print on oiled cloth; dry; cover with a three-colour pattern in Alizarin pink, Methylene blue, and Pigment grey (lampblack and albumen), or any other similar Basic and Pigment colours; steam one hour, wash, fix, and soap.

The oxalate of antimony resist (Resist B.T. II.) will also give a good white under either Alizarin or Basic colours (or both), but not under strong Pigment colours.

Resists under Iron and Aluminium Mordants.

These have already been dealt with under the Madder Style (Dyed Styles, *q.v.*).

Resist Effects under Insoluble Azoic Colours produced on the Fibre.

White and coloured reserve or resist effects are produced under this important class of colouring matters by printing, on naphthol-prepared cloth, either (*a*) reducing agents like stannous salts and alkaline sulphites, which reduce the diazo compounds, or (*b*) substances like the persulphates and citric and tartaric acids, which greatly retard, or counteract entirely, the coupling of the naphthol with the diazo compounds. Tannic acid is also an efficient resisting agent ; and although it is unsuitable for white resists, it affords a valuable means for the production of dark, rich Basic colour resist effects, fast to washing and soaping.

In addition to the above-mentioned substances, various insoluble bodies, such as China clay, waxes, and fats, are often incorporated with the resist pastes, especially those used for white resists. They act mechanically, and exercise a beneficial influence upon the perfectness of the resist and the purity of the white.

There are five methods in general use for the resisting of dyed insoluble Azoic colours :—

(1) Tin Resists.
(2) Sulphite Resists.
(3) Tannin Resists.
(4) Persulphate Resists.
(5) Wax Resists.

Strong caustic soda has also been tried as a resist for insoluble Azoic dyes. Its action depends upon the conversion of the diazo compound into a nitrosamine.

The preparation of the cloth in naphtholate of soda, and the subsequent dyeing, are carried out with the naphthol prepares and the diazo solutions already given in the section on Dyeing, under the heading of "Insoluble Azoic Colours."

Tin Resists.

The white and coloured resists obtained, under dyed Azoic colours, by means of tin salts, are produced in larger quantities than any similar style executed by other methods.

Stannous salts, and particularly stannous chloride (tin crystals), exercise a powerful action upon diazo compounds, which they reduce to hydrazines, bodies incapable of combining with β-naphthol.

Used alone, stannous chloride, while giving a perfect resist, imparts an undesirable yellow tinge to the white cloth, which cannot easily be cleared. The addition of organic acids—citric and tartaric—obviates this defect ; and as such acids are themselves moderately good resisting agents, they generally form one of the ingredients of Tin Resists of all kinds. To obtain the best results, the tin crystals employed should be fresh and free from all oxidation products ; the salt must be readily soluble, and have no appearance of white

efflorescence. Needless to say, it ought also to be as white as possible; any yellowish appearance is certain to give dirty whites, and flat, dull shades of colour.

For coloured resists, stannous chloride can be added to almost any of the Basic colour tannin printing pastes, and in certain cases to Chrome yellow or orange and Chrome green (Guignet's green). With the last three, somewhat *looser* colours are obtained, since the addition of albumen is out of the question; but taking this into account, the colours are remarkably fast to washing—much more so than if printed on plain white cloth under similar conditions. Naphthol prepares containing antimony salts are always employed for Basic colour resists, and are, moreover, the best in all circumstances, as they are less liable to develop brown stains on drying.

White Resist T.A.

500	grms.	50 per cent. gum Senegal solution.
400	,,	stannous chloride.
100	,,	tartaric acid.
1000		

White Resist T.B.

600	grms.	glue-starch thickening.
100	,,	China clay.
50	,,	tartaric acid.

Beat the clay into the paste; add the acid, and heat till it is dissolved; cool, and add—

250	grms.	stannous chloride.
1000		

Glue-Starch Thickening.

100	grms.	glue.
200	,,	water. Soak till soft, then add—
250	,,	acetic acid 9° Tw.
90	,,	paraffin wax.
285	,,	water.
75	,,	starch.
1000		Boil the whole until the glue is dissolved, and then cool.

Resist D. (to resist both the ground and the basic colour reserves).

100	grms.	British gum.
250	,,	water.
300	,,	sodium tartar emetic.
100	,,	zinc sulphate.
50	,,	tartaric acid.

Boil, cool, and add—

200	grms.	stannous chloride.
1000		

Resist D. is used chiefly for small white objects in the blue and red style.

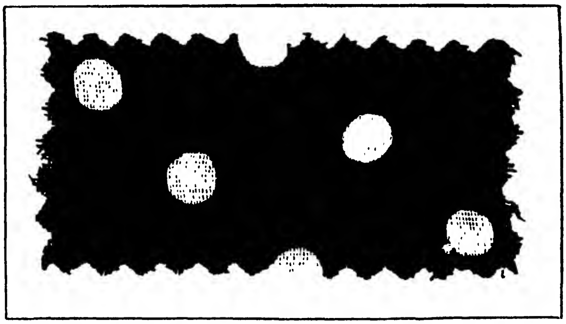
Colour Resists with Basic Dyestuffs.

Standard Pastes.	Red.	Pink.	Orange.	Yellow.	Blue.	Green.
Rhodamine 6 G. extra	25	10	5	..	..	..
Thioflavine T.	5	..	15	20	..	..
Pure blue II. (B.A.S.F.)	..	..	..	..	12·5	..
Brilliant green	..	..	..	..	..	13
Auramine G.	..	..	..	..	..	20
New methylene blue N.	..	..	..	..	12·5	..
Citric acid	25	25	25	25	25	25
Acetic acid 9° Tw.	200	200	200	200	250	200
Starch	100	120	100	100	100	100
Water	45	105	155	155	100	142
6 per cent tragacanth	100	140	100	100	100	100
Boil, cool, and add—						
50 per cent. tannic solution (in acetic acid)	300	200	200	200	200	200
	800	800	800	800	800	800

For Printing take :— {800 grms. above colour pastes.
{200 ,, stannous chloride.

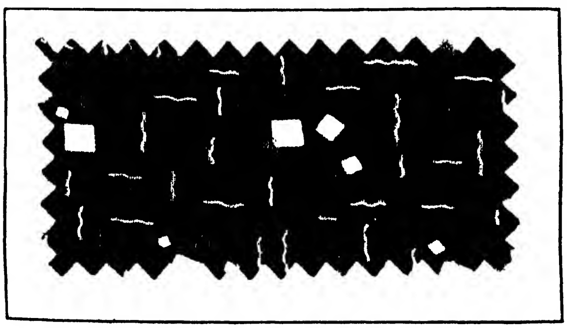
1000

Other Basic colours, such as Victoria blue, Auramine O., Auramine conc., Marine blue, Phosphine, etc., may be also applied according to the formulæ given above.



Tin resists under Paranitraniline Red.

The white and coloured resists are printed on cloth prepared in a 3 per cent. solution of β-naphthol containing 1 per cent. of tartar emetic, dried carefully in hot air or over rather cool cylinders, to prevent the tendering of the fibre, and then passed through various diazo solutions, according to the shade of ground required. After dyeing, the goods are well washed, soaped, washed, and dried. The run through the diazo compound constitutes the dyeing, and is usually carried out in a specially designed machine, to be described later.



Resists under α-Naphthylamine Claret.

A type of the Pigment Resists is the following :—

Resist Yellow C.

{300 grms. Chrome yellow paste.
{ 75 grms. glycerine.
{425 grms. 6 per cent. tragacanth thickening.
{200 grms. stannous chloride.

1000

Print exactly as for the preceding. Dry, dye, wash, etc.

Sulphite Resists.

WHITE K.S.:—	680	grms.	bisulphite of soda $66\frac{1}{2}°$ Tw.
	170	,,	water.
	85	,,	potassium carbonate (65 per cent. K_2CO_3).
Boil to expel carbonic acid, cool, and add—			
	100	grms.	starch.
	50	,,	British gum.
Make up to	1000		Boil and cool.
WHITE K.S.Z.:—	100	grms.	water.
	200	,,	zinc oxide.
	50	,,	starch.
	115	,,	50 per cent. gum Senegal solution.
	5	,,	paraffin wax.
	30	,,	Turkey-red oil 40 per cent.
Boil, cool, and add—			
	500	,,	potassium sulphite 105° Tw.
	1000		
WHITE K.S.M.:—	800	grms.	potassium sulphite 105° Tw.
	200	,,	British gum.
	1000		Boil and cool.

Coloured sulphite resists with pigments are based on the following type:—

BLUE:—	250	grms.	Ultramarine blue.
	40	,,	glycerine.
	160	,,	water. Beat up to a paste, and add—
	150	,,	6 per cent. tragacanth thickening.
	150	,,	50 per cent. albumen solution.
	250	,,	potassium sulphite 105° Tw.
	1000		

Sulphite resists are printed on naphtholated cloth, dried, and then dyed, etc., as usual. Coloured resists are given a quick run through the rapid ager to fix the pigment, and afterwards treated as above.

Under Paranitraniline red, sulphites give a better white than tin crystals, but under α-Naphthylamine clarets the reverse is the case.

Tannin Resists (Rollfs & Co., Germ. Pat. 113238).

Owing to the fact that tannic acid does not give a pure white resist under the Azoic colours, the tannin resists are only suitable for the production of *dark rich colourings* in blue, green, pink, and yellow, in combination with, and on grounds of, various Azoic colours. For this style of work, however, they are much superior to the coloured tin resists, which, at their best, are only capable of yielding light and moderately fast shades, since the unavoidable precipitation of the colour lake—a double tannate of tin and colour base—in Tin Resists precludes the possibility of obtaining dark colours of sufficient fastness to washing by this method. On the contrary, with Tannin Resists no such precipitation takes place until the printed goods are steamed, so that the colour lake, being produced on the fibre itself, possesses the maximum degree

of fastness to soaping. In order to secure the most permanent results, the Tannin Resists are, for the most part, printed on naphthol prepares containing alumina and tartar emetic, both of which form insoluble tannates. The fastness of the colours may also be increased by a run through tartar emetic, after dyeing in the diazo solutions; but, as a rule, this is not necessary.

A suitable naphthol prepare is the following:—

NAPHTHOL PREPARE.

I.	25	grms.	β-naphthol R.
	40	,,	caustic soda 36° Tw.
	120	,,	hot water.
II.	25	,,	aluminium hydrate 50 per cent. paste.
	20	,,	caustic soda 36° Tw.
	250	,,	hot water.
	30	,,	ricinoleate of soda 50 per cent.
	75	,,	6 per cent. tragacanth thickening.
III.	10	,,	tartar emetic.
	12	,,	tartaric acid.
	50	,,	glycerine.
	80	,,	caustic soda 36° Tw.
	250	,,	water. Make the whole to—
	1 litre		

Mix I., II., and III., and heat gently until the solution is clear; then add water to make up to volume.

On cloth prepared in the above solution, the following resist colours may be printed:—

TANNIN RESIST COLOURS.

	ROSE T.R.	YELLOW T.R.	GREEN T.R.	BLUE T.R.
Rhodamine 6 G. extra	15	..	..	..
Auramine (concentrated)	..	25	15	..
New methylene blue N.	..	..	5	..
Marine blue S. (Geigy)	..	..	..	12·5
Brilliant green cryst. extra	..	..	5	..
Pure blue II. (B.A.S.F.)	..	..	..	12·5
Crystal violet O.	..	..	..	5
Acetic acid 9° Tw.	250	250	250	240
Acetin	50	50	50	50
Water	240	230	230	200
Starch	120	120	120	120
6 per cent. tragacanth	100	100	100	100
Tartaric acid	25	25	25	10
Oxalic acid	..	..	..	50
Boil, cool, and add—				
Tannin 50 per cent. sol. (in acetic acid)	200	200	200	200
	1000	1000	1000	1000

Print on naphthol-prepared cloth, dry, and steam 2 minutes in the rapid ager; develop the ground shade by a run through the required diazo solution, and then pass, if required, through a 2 per cent. solution of tartar emetic at 40°–50° C.; wash well, soap, and dry.

Other naphthol prepares may be used, but the above is one of the best for resisting the detrimental action of hot steam. In order further to reduce the unfavourable influence of steaming on the depth of the Azoic colour grounds, the goods must be prevented from coming in contact with the copper guide rollers in the rapid ager. Hot metal, especially in conjunction with steam, acts injuriously on the naphthol prepare, and gives rise to irregularities in the dyeing operation. For this reason, therefore, the cloth is best insulated from the guide rollers by fixing lengthwise on the latter a series of wooden bars, thus converting them into a sort of wince.

If it be required to work a resist white in combination with tannin resists, the White Resist K.S.Z. (Sulphite) is suitable. On Para red grounds, claret and black are obtained by printing α-Naphthylamine claret and Nigrophor respectively; a brown, by printing a thickened solution of Brown salt R. or G. On claret grounds, only a fairly good red is obtainable, and that by employing a tannin resist colour containing Rhodamine and Auramine, or other suitable yellow and red Basic dyestuffs. All these Azoic colours may be printed on naphthol grounds along with any class of resists, be they tin, sulphite, or tannin; but the tannin reserves cannot be employed along with tin resists since the latter *cannot* be steamed without tendering the fabric.

For a white resist under both the Azoic colour ground and its printed resist, *Resist D.* (sodium tartar emetic and tin crystals—see Tin Resists) is first applied to the naphtholated cloth, which is then dried and treated in the way described above. Care must be taken to reduce the quantity of tin crystals to its lowest effective point, otherwise, in steaming, the cloth is liable to be tendered. For this reason only small objects, spots and the like, are printed in Resist D.

Another way of working the tannin resist method is to print the colours on white cloth unprepared in any way; steam for an hour, and then, without washing, to prepare the goods in naphthol, dry and dye up at once in the diazo solutions. The preparation in naphthol, if not done on the printing machine, is carried out on a padding mangle, the bottom squeezing bowl of which works partly immersed in the naphthol solution; the goods pass straight through the nip, face downwards, and are impregnated by the liquor carried up by the bottom bowl, which, as a rule, is wrapped with several thicknesses of calico, in order to transfer a sufficient quantity of liquor to the cloth. By this method of working, it is not possible to print insoluble Azoic colours in combination with the resists.

Persulphate Resists.

The employment of persulphates as reserving agents is, in practice, restricted to one style, namely, the production of blue and red effects, obtained by printing a Dianisidine copper blue containing a persulphate on naphtholated cloth, followed by a run through paranitrodiazobenzene for the development of Para red (Schäppi).

The presence of persulphates in the blue printing paste has no injurious effect upon the coupling of the tetrazo compounds of Dianisidine with the naphthol in the prepare; but, under the influence of the heat in the drying apparatus attached to the printing machine, the persulphate oxidises any excess of naphthol that may remain on the printed parts, so that no Para red forms on these in the subsequent developing bath. The blue naphthol Azoic dyestuff of Dianisidine, already existing on the fibre, remains unaffected in drying, and consequently the ultimate result is a blue pattern on a red ground, or *vice versa*, according to the pattern printed in blue.

In order to prevent the dulling of the red by the copper salt which dissolves out of the blue, the usual developing bath of diazo-*p*-nitraniline is modified by the addition of ammonium oxalate, and the same addition is made to the final soaping liquors. The goods, too, are developed by passing straight through the nip of the mangle bowls, instead of through the liquor in the box beneath.

The following recipes have been used successfully in practice :—

NAPHTHOL PREPARE B.R.

25	grms.	β-naphthol.
40	,,	caustic soda 36° Tw.
850	,,	hot water.
50	,,	Turkey-red oil 40 per cent.
35	,,	acetate of soda. Make up to—
1 litre		

BLUE B.R.

16·5	grms.	Dianisidine salt (powder).
100	,,	hot water.
12	,,	hydrochloric acid 30° Tw. Dissolve, cool, and add—
200	,,	ice.
31	,,	nitrite of soda solution 25 per cent. $NaNO_2$.

Allow to stand some time, then add—

540·5	grms.	thick flour paste.
50	,,	persulphate of potash crystals.
50	,,	cupric chloride 75° Tw.
1000		Make up to 1 litre with a little water or thickening.

RED DEVELOPING BATH.

14	grms.	Paranitraniline.
75	,,	hot water.
26·4	,,	hydrochloric acid 30° Tw.

Heat till dissolved, then cool, and add—

150 grms. ice.

And then, at not above 2° C.,—

29 grms. 25 per cent. solution of nitrite of soda.

Allow to act 15 minutes, stirring at frequent intervals ; then strain and add—

500	grms.	cold water.
30	,,	acetate of soda.
20	,,	oxalate of ammonia crystals, and sufficient water to bring the whole up to 1 litre.
1 litre		

On cloth padded in Naphthol Prepare B.R., print Blue B.R., dry quickly over cylinders or in hot air, cool the goods, and pass them at once through the above developing bath, wash them well in the open width with plenty of running water, and then soap at 60° C., also in the open width, through a solution of soap containing 0·5 per cent. soap and 0·2 per cent. oxalate of ammonia ; wash, and again soap at 60° C. for 15 minutes in the rope state, and with a soap liquor of the same composition ; finally, wash well and dry.

If the above Dianisidine blue resist be printed on Naphthol A.S. instead of upon β-naphthol, and the red developed with Fast Red Base G.L. (metanitroparatoluidine) instead of with paranitraniline, a faster blue is obtained, and, at the same time, there is no necessity to add oxalate of ammonia either to the dye bath or the following soap bath, as Fast Red Base G.L. is scarcely affected by copper salts. Fast Blue B. Salt, which is already tetrazotised, may replace Dianisidine in this and every other instance.

With the single exception of persulphate resists, all other insoluble Azoic colour resist styles, on β-naphthol, are dyed with the several diazo solutions for which formulæ have been given under The Dyeing of Plain Shades with Azoic Colours.

For red grounds :—Paranitraniline.
,, claret ,, a-Naphthylamine.
,, scarlet ,, Chloranisidine.
,, orange ,, o-Nitrotoluidine.
,, chocolate ,, Benzidine.
,, brown ,, mixtures of Benzidine and o-Nitrotoluidine.

In all insoluble Azoic colour resist styles the dyeing of the ground, unlike that of plain shades in which the goods pass through the dye liquor, is best carried out by running the printed pieces directly between the bowls of the

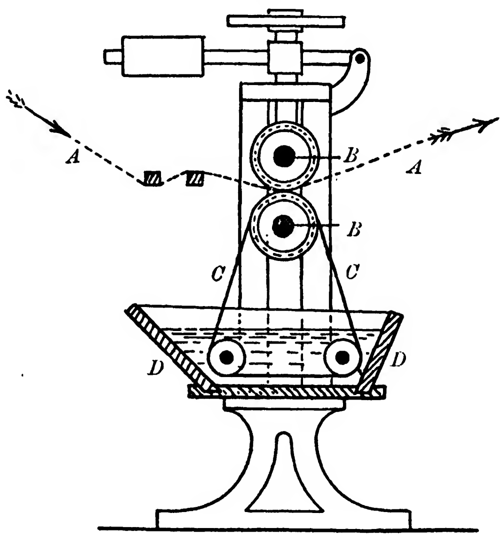


FIG. 82.—Padding machine for Azoic colour resist styles.

padding mangle, the dye liquor being supplied to them either by means of a perforated pipe, or from an endless woollen blanket circulating between the mangle bowls and the liquor in the box below. In both cases the washing, etc., arrangements are the same. The two accompanying diagrammatic sketches will make the working details of these machines sufficiently clear.

In fig. 82 A A represents the printed cloth passing through the machine, printed side to the lower bowl ; B B the mangle bowls, both of sycamore, wrapped with several thicknesses of calico ; C C the woollen colour-feeding blanket ; and D D the colour box beneath.

In fig. 83, which shows in section the full arrangement of a dyeing machine for reserve styles, A A A represents the cloth running in the direction of the

arrow; B B, the mangle bowls, the *upper one* of sycamore wrapped with calico, the lower one of copper working half immersed in the dye liquor which runs off the cloth; C, the perforated pipe which supplies the dye liquor to the cloth; D, a trough to catch the excess of liquor; O, the overflow pipe of D communicating with the tub F, in which the dye liquor is collected, and from which it is ladled again into the vessel connected with the perforated supply pipe C; E, a brass doctor to clear the copper bowl B of any colour that may be transferred to it from the printed cloth; G G, hot-water washing becks; H H, series of hot-water spirt pipes; S, soaping beck; M M M M M, squeezing bowls, the top one of rubber, the bottom one of copper; W, a cold-water washing beck fitted with squeezing bowls P.

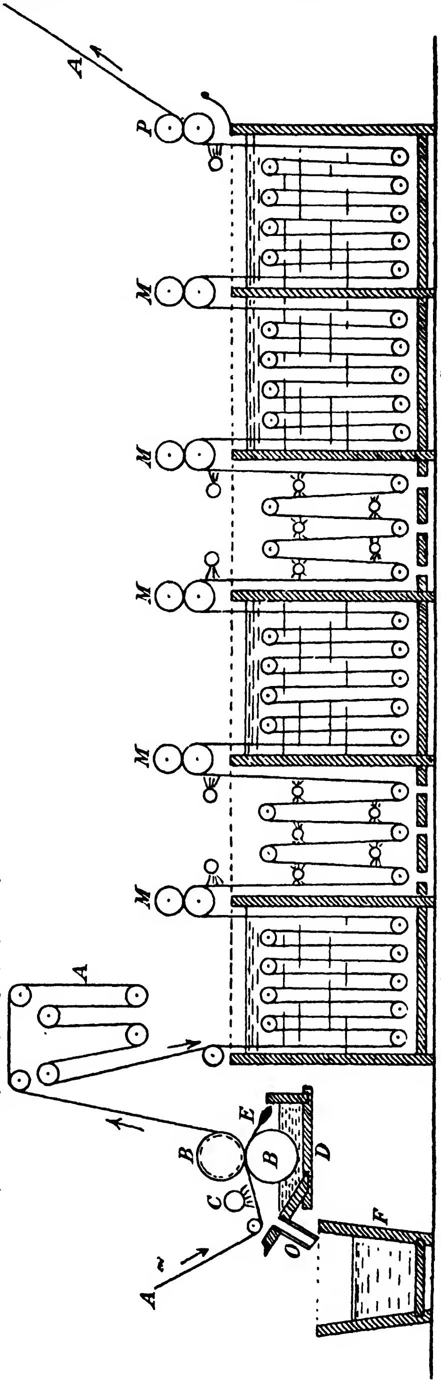


Fig. 83.—Dyeing and washing machines for Azoic colour resist styles.

The cloth, after passing through the first pair of bowls, is allowed to travel some distance in the air, in order to allow time for the naphthol Azoic colour to develop completely. The rest of the diagram is self-explanatory. It may be noted that each pair of squeezing bowls is fitted with screw and lever pressure, so that they may be regulated as required for thicker and thinner cloth.

The use of padding mangles constructed on lines similar to the above overcomes two of the most serious difficulties that are likely to be encountered in the dyeing of Azoic resist styles. In the first place, regularity and evenness of colour, both as regards depth and shade, is ensured by reason of the fact that the dye liquor, being used in small quantities, must be freshened up at very short intervals, and consequently the accumulation of tin salts in the bath is prevented, and with it the destruction of the diazo solution; secondly, the marking off of the printed pattern on the ground colour is also avoided by the manner in which the cloth runs through the machine. Being passed through the bowls face downwards, any marking

off takes place on the feeding blanket or the lower copper bowl: from the former, the stannous chloride is washed off or neutralised in the dye liquor, which suffers a little, but is renewed too rapidly to show any appreciable loss of tinctorial strength; and from the latter (copper bowl), the stannous chloride, colour lakes, and thickening are either removed in the same way or scraped off altogether by the brass doctor (E, fig. 83).

Wax Resists.

Excellent white resist effects are obtained under insoluble Azoic colours by printing mixtures of wax, resin, British gum, and an acid, or acid salt, on white unprepared cloth. After drying, the cloth is prepared in β-naphthol by padding straight through the nip of a mangle, the bottom bowl of which works in the preparing liquor. From the mangle it passes directly on to the drying cans of a drying machine, and is then ready for dyeing in any desired diazo solution. It is preferable to perform the dyeing at once, and by the same means as those employed for preparing—by padding directly through the nip of a mangle—except that a thorough wash must be provided for before proceeding to dry the goods. In works where large quantities of single colour white resists are produced, the operations of dyeing, washing, and drying are carried out in a continuous manner.

The wax-resist process was one of the earliest employed for obtaining white patterns on Azoic colour grounds, but, although for this particular purpose it leaves nothing to be desired, it gradually declined in favour because it is not easily applicable to multicolour styles, which are best printed on naphtholated cloth. The padding of resist colours containing reducing agents, etc., through solutions of β-naphthol, presents difficulties, in practice, which render it preferable to make use of one or other of the processes described on previous pages.

The high price of stannous chloride and hydrosulphites has, however, brought about a revival of the use of the old wax resists for all classes of work to which they are adapted; and at the present time they are again employed by calico printers for single-colour patterns. Apart from their comparative cheapness, they possess distinct advantages in the way of giving perfect whites —a result due to the fact that the cloth is protected from both the naphthol solution and the diazo solution—and in permitting of the cloth being printed at any convenient time. If stored, after printing, in a dry and not too warm place, the goods may be kept, without detriment, until a sufficient quantity is ready for a day's run of preparing and dyeing. On the other hand, naphtholated cloth must be printed as soon as possible after preparing, even if there are only a few pieces required, and the dyeing must also be proceeded with at once, if satisfactory results are to be secured. Hence, wherever it can be introduced, a wax resist is preferred to any other.

The wax resists act both chemically and mechanically—chemically by reason of their acid, which throws the β-naphthol out of solution; mechanically by covering the fibre with a protecting layer of wax and resin.

The recipe given below represents a typical wax resist:

RESIST WHITE W.X.

$$\left\{\begin{array}{lll} 30 & \text{grms.} & \text{paraffin wax.} \\ 30 & ,, & \text{resin.} \\ 200 & ,, & \text{water.} \end{array}\right.$$

Melt and add—

330 grms. British gum.

Boil and add—

$\begin{cases} \text{220 grms. citric acid.} \\ \text{400 ,, water.} \end{cases}$

Boil again and make up to—

1 litre

Print the warm (not hot) resist on white bleached cloth, dry, prepare as described in β-naphthol, dry and pass through diazotised α-naphthylamine, wash well, soap, and dry up.

Modifications of the above resist consist in the addition of glue and (especially for Para reds) of stannous chloride. When the latter is used it is necessary to sour before soaping.

Modifications of the Azoic Colour Resist Style.

There are two useful methods of producing resist effects under figured or patterned grounds of insoluble Azoic colours. In the first, used mainly for white resists, plain bleached cloth is first printed with a tin or a sulphite resist white, then dried gently and *covered* with a fine all-over pattern in a thickened solution of β-naphthol. Hereafter the process is identical with that for dyed grounds described above. The naphthol printed pieces are dyed in the padding machine with any suitable diazo solution, well washed, soured if necessary to clear the white, well washed again, soaped, washed, and dried. In the second and more largely employed method, the goods are prepared in the ordinary way with naphthol. After drying, white and any sort or number of coloured resists are printed, and then the whole is over-printed or covered with a fine pattern (check, zephyr, fine line or delicate scroll) or a blotch in either Red P.N. or Claret A.N., according as Para red or Naphthylamine claret is required in the ground. Goods printed with tin resist colours are now passed at once through tartar emetic (1½ grm. per litre), well washed, soaped, washed, and dried. Tannin resists and coloured sulphite-pigment-albumen resists require steaming for 2–3 minutes in the rapid ager before they are washed and soaped. Tannin resists are fixed like tin resists in tartar emetic before washing. By operating in this way a great variety of very pretty fancy effects are easily obtainable.

By combining the Azoic resist style with the chlorate discharge on Indigo it is possible to obtain many curious mixed effects in red, chocolate, blue, white, and yellow, effects which are suitable for the Eastern and West Coast of Africa markets. These styles depend upon the opposite behaviour of Indigo and Para red towards oxidising and acid reducing agents. Indigo is destroyed by the former and practically unaffected by the latter, whereas Para red is prevented from developing by the latter, and, when once formed, is almost entirely unacted upon by the former at the strength used to discharge Indigo.

The following is a résumé of the operations necessary to the production of combined resist and discharge effects on Indigo and Para red:—

(1) Dye the cloth a light shade of Indigo. Dry.

(2) Prepare in β-naphthol. Dry.

(3) Print on a stannous chloride resist white. (White Resist T.B., p. 740.) Dry.

(4) Dye in paranitrodiazobenzene (14 grms. paranitraniline per litre). Wash, sour, wash, soap, wash, and dry. At this stage the goods present the appearance of a dark chocolate pattern on a light blue ground. The chocolate results from the superposition of red on blue.

(5) Print Chlorate white and Chlorate yellow (see below) with a two-colour pattern of such a design as will ensure the falling of the two colours over both the blue and chocolate.

Chlorate Discharges.	White.	Yellow.
Water	475 grms.	425 grms.
British gum	250 ,,	180 ,,
Chlorate of soda	100 ,,	100 ,,
Lead nitrate	..	175 ,,
Boil and add—		
Citric acid	50 ,,	50 ,,
Cool and add—		
Red prussiate of potash	25 ,,	20 ,,
Water	100 ,,	50 ,,
	1000	1000

(6) Steam 4–5 minutes, or less, in the rapid ager. This discharges the Indigo, leaving, at this stage, a red where the colours fall on the chocolate, and a white where they fall on the blue.

(7) Pass through a solution of sulphate of soda (150 grms. Glauber salt, and 25 grms. sulphuric acid, 168° Tw., per litre) at 40° C.; wash well.

(8) Chrome in a ½ per cent. solution of bichromate of soda neutralised with ammonia; treat for 5–8 minutes at 40° C., wash well, and dry if for yellow. If orange is required, treat further for 1 minute in a bath containing 10 grms. bichromate and 40 grms. quicklime per litre of water at the boil; wash again and dry.

If the first and second patterns consist of longitudinal and transverse stripes respectively, the ultimate effect of the above series of operations will be that of a six-colour check, namely, the original blue of the ground, white and yellow (or orange) where the blue has been discharged, red where the chlorate white has crossed the chocolate formed by red falling over blue, and a reddish-orange or a scarlet where the chlorate yellow (or orange) is superposed on red.

A similar effect is attained by printing Para red on the naphtholated Indigo-dyed cloth instead of the Resist White T.B. With the exception of dyeing, which in this case is unnecessary, the rest of the process is precisely as above.

For many years the several resist processes just described afforded the only means of obtaining coloured reserves under dyed grounds of Insoluble Azoic colours produced on the fibre and, as such, they enjoyed an exclusive vogue for a long period. Since the introduction of stable hydrosulphite discharging agents, however, and the consequent development of discharging processes, the importance of resist methods has gradually declined, and to-day they are confined, for the most part, to the production of fast Azoic colour resists, of great brilliancy, on Variamine blue grounds, a special and important style which it is impossible to produce by any method of discharging. A few cheap shipping lines on low cloth, *e.g.* Basic colour resists, of inferior fastness, under Paranitraniline red and α-Naphthylamine claret, are still printed with tin salt or sulphite resist colours; but for better-class work of this type on other grounds all such effects are now preferably obtained in fast colours by discharging various Naphthol A.S. combinations, as already described elsewhere in this work.

Resists under Variamine Blue.

Variamine blue B., in combination with Naphthols of the A.S. group, gives particularly fine shades of Navy blue of excellent all-round fastness.

Variamine blue dyeings are of special interest in Resist printing on account of the ease and certainty with which they may be reserved by acidic substances —a property which allows of Azoic colours being utilised, in a simple straightforward manner, for the production of the ever-popular " Blue-Red style " and for many other exceedingly bright and fast resists under a dark blue ground.

The advantages attaching to the use of Variamine blue for these purposes are, that block printing, the preparation of complicated and badly working special resist pastes, and the tedious and delicate operations of vat dyeing, are dispensed with, the resists being printed by machine to give perfectly sharp impressions which are not liable to run or form halos during subsequent treatment of the goods. Moreover, Variamine blue is more economical than other fast blues, be they Indigo, Indigosol, or Indanthrene, and, if not equal to the last in fastness, is yet sufficiently fast to satisfy high standards.

Resist effects are obtained under Variamine blue by printing, on naphtholated cloth, various acid salts, non-volatile organic acids, salts which react acid in steaming, and reducing salts, of which the most generally useful in practice are: aluminium sulphate, sodium bisulphite, potassium sulphite, ammonium oxalate, and ammonium sulphocyanide. Coloured resists are produced from mixtures of these salts with appropriate colouring matters, together with the necessary materials for development or fixation. Thus resists are prepared from:—

(1) Azoic colours (diazo-solutions) with aluminium sulphate ;
(2) Indanthrenes with potassium sulphite ;
(3) Indigosols with ammonium oxalate or sulphocyanide, sodium bisulphite, and/or potassium sulphite ;

there being added, in each case, the essential adjuncts to fixation as noted above, and given in detail in the following descriptions of the processes.

General Working Method.—After the naphthol-prepared goods have been printed with the resist colours, and, if necessary, steamed for 5–8 minutes, they are passed directly, printed side uppermost, between the wrapped bowls of a two-bowl padding mangle, the bottom bowl of which is partly immersed in a solution of diazotised Variamine blue B. base or of Variamine blue salt B. (see fig. 84).

From the squeezing bowls of the padding machine the goods are passed over a series of airing rollers, or aired on a " creeper," for at least 1 minute in order to allow complete coupling to take place. In practice 2–3 minutes are frequently found to be necessary to ensure the full development of the blue ; in any case it is advisable to overdo rather than underdo the air passage.[1] After airing, the goods, in the full-open width, are passed through a hot acid bath (10 c.c. sulphuric acid, 168° Tw., per litre at 140° F.), and then well washed in the rope form in hot and cold water successively until the wash water is no longer yellowish, *i.e.* until all excess of dye liquor has been completely washed out.

Here again it has been found in practice that a short hot souring in the open width followed by washing is *not sufficient* to yield clear resists when working in bulk. If the whole of the excess of dye liquor is not removed

[1] The air passage may be omitted if the goods are padded in the developing machine shown in fig. 84. A short steaming brings about the rapid coupling of the diazo body with the naphthol, as described in the section on Discharges on Naphthol A.S. Combinations.

during the acid treatment the residue is carried forward into the washing machines, and there, as soon as the acid liquor becomes sufficiently diluted with wash water, it couples up with the free naphthol still remaining under the printed resists, and thus imparts a light blue stain or "scum" to the whole printed surface of the goods — a stain which, of course, dulls the illuminating colours considerably and ruins the white resists irretrievably. To avoid this disaster it is only necessary to wash out *all excess dye liquor in an acid bath,* and to this end the goods, after being soured in the acid tank of the padding machine, are again soured thoroughly for 10–15 minutes in a three-beck rope-washing machine (10 c.c. sulphuric acid, 168° Tw., per litre at 110°–120° F.). When the acid wash runs clear, and not until then, the goods are thoroughly washed in hot and cold water and then soaped at the boil for 10 minutes in—

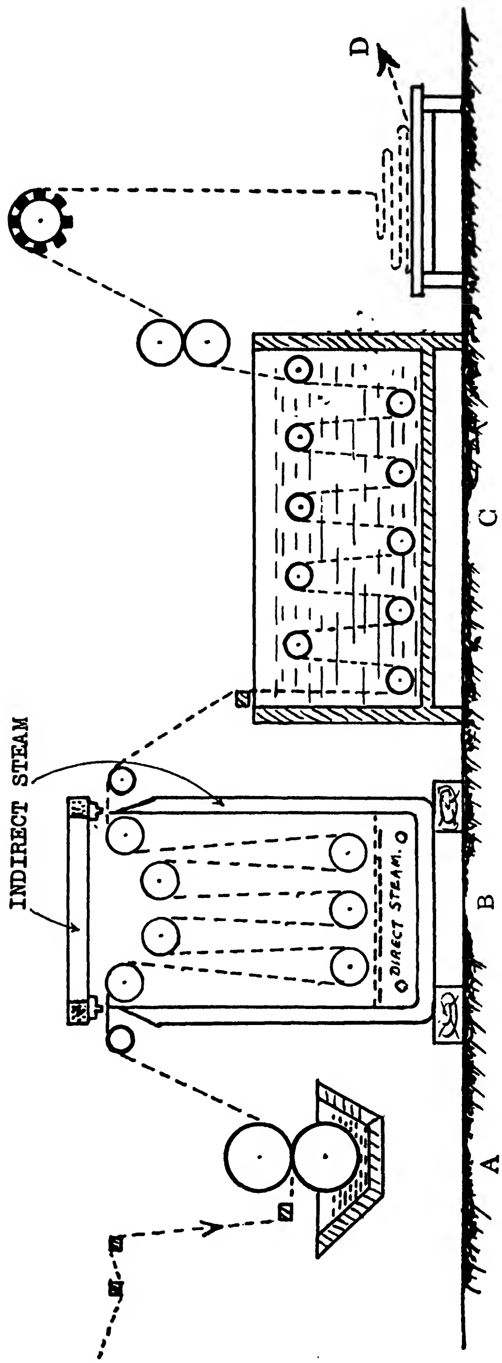


FIG. 84.—Developing machine for Variamine blue.
(A) Padding mangle. (B) Jacketed high-temperature steaming box.
(C) First souring box. (D) Forward to souring and washing becks.

$\left\{\begin{array}{l}\text{3 grms. soap ;}\\ \text{1 grm. soda-ash ;}\\ \text{1000 c.c. water;}\end{array}\right.$

washed again, and then dried.

A certain amount of naphthol remains in the cloth after souring and washing (precipitated by the acid treatment under the resists), and is removed completely only in the final soaping.

Souring, washing, and soaping are all carried out in the rope form, and may be arranged as a continuous process. Souring, however, is usually done in a separate machine.

A treatment in bisulphite of soda, in place of souring, has proved satisfactory in some hands, but it is a method that has not come into general use in this country.

Azoic Colour Resists.—For the production of the brilliant red and orange effects which are characteristic of Variamine blue resist styles, the Azoic colours are unsurpassed—in fact, they are indispensable. Their range is limited to reds, oranges, and medium to light blues, but as reds and oranges are by far the most important, and form part of practically every colouring, this limitation is of little moment, though naturally a complete range of colours would be desirable.

The lack of Azoic yellows, greens, and certain shades of blue, grey, brown, etc., is made good by the use of Vat dyestuffs (Indanthrenes, Indigosols, and the like).

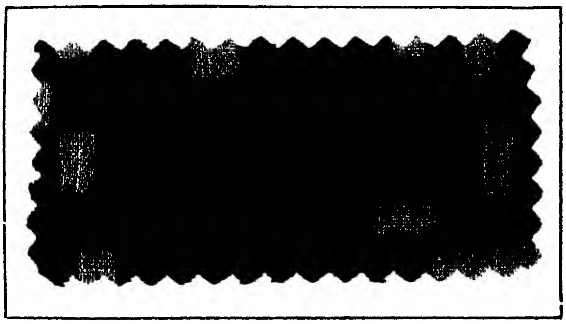
The Azoic colours yield fast colours of unrivalled richness and brilliancy; used alone, they dispense with steaming, and above all they are extremely simple in application. Resist colours are prepared merely by adding aluminium sulphate to the ordinary diazo-printing colours.

For resist printing the bases which have been found most useful in practice are:—

Fast red K.B. base	Fast orange G.C. base
,, ,, T.R. ,,	,, blue B.B. ,,
,, ,, salt 3 G.L.	

or the corresponding Fast Colour salts.

The following patterns, with particulars of their execution, will convey some idea of the wide scope of the Variamine blue resist style.



Naphthol A.S./Variamine Blue B., with Azoic Colour Resists (I.G.).

(1) The bleached cloth is prepared in:—

15 grms. Naphthol A.S.
20 c.c. Monopol Brilliant Oil.
22 c.c. caustic soda 62° Tw.

To 1000 c.c.

(2) Dry and print:—

Printing Colours:—

	Red.	Orange.	Blue.
Fast red salt T.R.	50 grms.	..	..
,, orange salt G.C.	..	60 grms.	..
,, blue salt B.B.	..	..	10 grms.
Water at 75°–85° F.	350 ,,	340 ,,	410 ,,
Starch-tragacanth paste	500 ,,	500 ,,	500 ,,
Aluminium sulphate 50 per cent. solution	100 ,,	100 ,,	80 ,,

1000 grms. each.

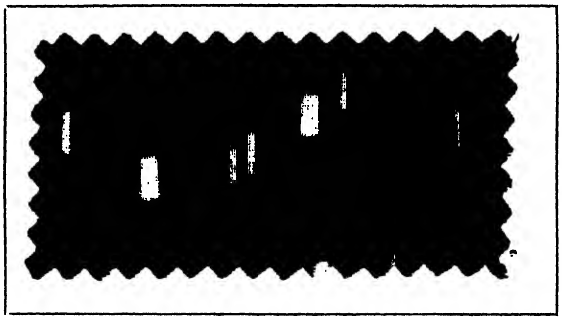
(3) After printing, dry and develop in the padding machine with:—

40 grms. Variamine blue salt B.
1000 c.c. water.

Air 2–3 minutes, sour in sulphuric acid (10 c.c. acid, 168° Tw., per litre) at 140° F. for 1–2 minutes in the open width in the padding machine tank (see fig. 84), sour in the rope form at 110°–120° F. for about 10 minutes, wash, soap at the boil, and dry as already described.

Indigosol Resists.—The Indigosols afford a ready and convenient means of obtaining a more or less complete colour range of resist effects on Variamine blue grounds. Several methods are available, of which the three most generally useful will be described.

(*a*) The *first method* bears a close resemblance to the process employed in the direct printing of Indigosols, and involves a short steaming operation, the object of which is twofold, viz. the development of the Indigosols by oxidation and the decomposition of the ammonium oxalate constituent with deposition of free oxalic acid on the fibre. The oxalic acid acts as a resist, and prevents the development of the blue ground during the subsequent padding in Variamine blue.



(I.G.)

Naphthol A.S./Variamine Blue, resisted with { Indigosol Green and Azoic Colours.

(1) Naphthol Prepare.

See preceding pattern.

(2) Dry and print:—

White Resist.

150–200	grms.	aluminium sulphate 50 per cent. solution.
350–300	,,	water.
500	,,	starch-tragacanth paste.
1000	grms.	

Orange Resist.

As preceding pattern.

Red Resist.

60	grms.	Fast red salt 3 G.L.
320	,,	water 75° F.
500	,,	starch-tragacanth paste.
50	,,	aluminium sulphate.
50	,,	water.
20	,,	Paradurol.
1000		

Green Resist (Indigosol).

30	grms.	Indigosol green I.B.A. paste.
30	,,	Indigosol yellow I.G.K.
50	,,	Glyecine A.
265	,,	water at 140° F.

Mix to a smooth paste and stir into—
500 grms. starch-tragacanth paste (neutral).

Heat to 140° F. for a time, cool, and add cold—

5	c.c.	ammonia 25 per cent.
35	grms.	ammonium oxalate, finely ground.
35	,,	sodium chlorate 1 : 2.
50	,,	ammonium vanadate 1 : 1000.
1000	grms.	

(3) After printing, steam for 5–8 minutes in the rapid ager, develop in Variamine blue salt B., air, sour, wash, and soap in the manner already described.

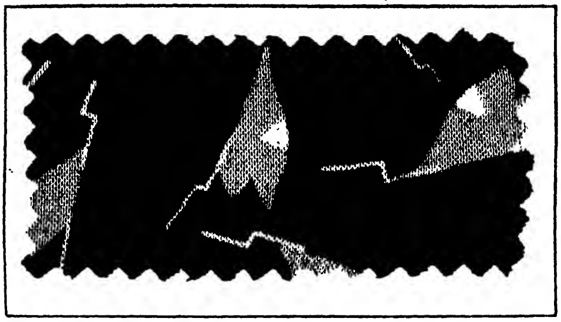
Other resist colours based on the same principles as the foregoing green will be found in the following table:—

	1.	2.	3.	4.	5.	6.	7.	8.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol Yellow H.C.G.	60	..	..	..	..	..	..	..
,, Golden Yellow I.G.K.	..	50	..	..	..	..	..	..
,, Orange H.R.	..	..	60	..	..	..	..	..
,, Pink I.R. Extra	..	..	..	40	..	..	..	..
,, Green I.B.A.	..	..	..	..	80	..	..	..
,, ,, A.B.	..	..	..	..	..	80	..	..
,, O. 6 B.	..	..	..	..	..	..	40	..
,, Printing Black I.B.	..	..	..	..	..	..	..	20
Glycecine A. or Fibrit D.	50	50	40	50	50	50	50	..
Solution Salt B.	..	..	40	50	..	50	..	..
Water	185	195	155	135	165	115	180	310
Tragacanth thickening	600	600	600	600	600	600	600	600
Heat until dissolved, then add—								
Ammonium oxalate in fine powder	35	35	35	35	35	35	60	20
Afterwards cool and add—								
Sodium chlorate 1 : 3	60	60	60	80	60	60	60	40
Vanadate 1 per cent.	10	10	10	10	10	10	10	10
	1000 grms.							

Sulphocyanide of ammonia may replace an equal weight of the oxalate in any of these recipes.

(*b*) In the *second method* of printing Indigosol resists on Variamine blue grounds, advantage is taken of the resisting properties of sulphites and bisulphites, and the steaming operation for the development of the resist colours is done away with, the necessary oxidation being obtained from chromic acid liberated during the subsequent hot acid treatment from lead chromate, which forms an essential ingredient of the printing colours.

An example of this method of working is as follows, and is illustrated by the accompanying pattern.



(I.G.)

Naphthol A.S.-E./Variamine Blue Salt F.G. resisted { White. Azoic Red. Indigosol Yellow.

(1) Prepare the goods, at a high temperature, in :—

{ 10 grms. Naphthol A.S.-E.
10 ,, Monopol Brilliant Oil.
15 c.c. caustic soda 72° Tw.
30 ,, methylated spirit.

Mix into a smooth paste and make up to—

1000 c.c. with boiling water.

Preparing temperature, 195°–212° F.

(2) Dry in the hot flue and print :—

WHITE RESIST.

300	grms.	aluminium sulphate 50 per cent. solution.
200	,,	water.
500	,,	starch-tragacanth paste.
1000		

RED RESIST.

50	grms.	Fast scarlet salt R.
75	,,	aluminium sulphate 50 per cent. solution.
375	,,	water.
500	,,	starch-tragacanth paste.
1000		

YELLOW RESIST (INDIGOSOL).

{ 80 grms. Indigosol yellow I.G.K.
70 ,, Fibrit D.
255 ,, hot water.

Dissolve and add to—

400 grms. starch-tragacanth paste.

Mix well, warm up, cool, and add—

65	grms.	sodium bisulphite 72° Tw.
10	,,	ammonium sulphocyanide.
120	,,	Chrome yellow 60 per cent. paste.
1000		

(3) After printing, the goods are developed in the padding mangle in—

{ 50 grms. Variamine blue salt F.G.
{ 1000 c.c. water

at a temperature of 77°–86° F., given an air passage of 1–2 minutes, then soured in the open width for ½ minute at 176° F. in—

{ 30 c.c. hydrochloric acid 32° Tw.
{ 1000 ,, water 176° F.,

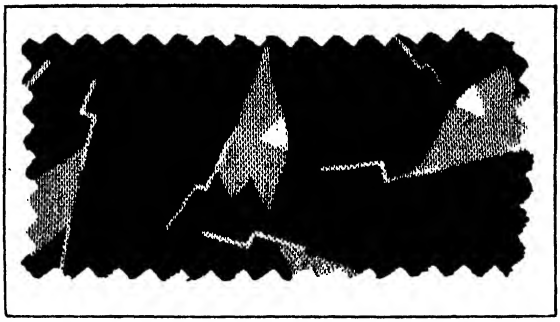
then soured again, using half the acid strength, in the rope form, and finally washed and soaped at the boil as usual.

Other Indigosols suitable for the lead chromate process are prepared for printing as under :—

INDIGOSOL-LEAD CHROMATE RESISTS.

	1.	2.	3.	4.	5.
	grms.	grms.	grms.	grms.	grms.
Indigosol Golden Yellow I.G.K.	80	..	..	..	..
,, Green I.B.A.	..	80	..	..	..
,, Pink I.R. Extra	..	..	50	..	..
,, Printing Violet I.B.B.F.	..	..	..	80	..
,, Violet A.Z.B.	..	..	..	..	80
Fibrit D.	70	80	30	30	80
Glycerine	..	..	50	..	..
Solution Salt B.	..	..	30	..	..
Hot water	255	245	235	330	270
Neutral starch-tragacanth thickening	400	400	400	400	400
Sodium bisulphite 71° Tw.	65	..	..	30	..
Potassium sulphite 90° Tw.	..	60	70	..	35
Ammonium sulphocyanide	10	15	15	10	15
Lead chromate paste 60 per cent.	120	120	120	120	120
	1000 grms.				

	6.	7.	8.	9.	10.
	grms.	grms.	grms.	grms.	grms.
Indigosol O. 4 B.	40	..	..	..	..
,, Red Violet I.R.H..	..	80	..	..	..
,, Printing Purple I.R.	..	..	60	..	..
,, Brown I.R.R.D.	..	..	..	40	..
,, Printing Black I.B.	..	..	..	..	15
Fibrit D.	60	50	70	30	..
Glycerine	..	..	..	..	30
Solution Salt B.	..	30	..	30	30
Hot water	330	255	280	350	335
Neutral starch-tragacanth thickening	400	400	400	400	400
Sodium bisulphite 71° Tw.	..	..	60	20	..
Potassium sulphite 90° Tw.	40	55	..	..	60
Ammonium sulphocyanide	10	10	10	10	10
Lead chromate paste 60 per cent.	120	120	120	120	120
	1000 grms.				



(I.G.)

Naphthol A.S.-E./Variamine Blue Salt F.G. resisted { White. Azoic Red. Indigosol Yellow.

(1) Prepare the goods, at a high temperature, in :—

10	grms.	Naphthol A.S.-E.
10	,,	Monopol Brilliant Oil.
15	c.c.	caustic soda 72° Tw.
30	,,	methylated spirit.

Mix into a smooth paste and make up to—

1000 c.c. with boiling water.

Preparing temperature, 195°–212° F.

(2) Dry in the hot flue and print :—

WHITE RESIST.

300	grms.	aluminium sulphate 50 per cent. solution.
200	,,	water.
500	,,	starch-tragacanth paste.
1000		

RED RESIST.

50	grms.	Fast scarlet salt R.
75	,,	aluminium sulphate 50 per cent. solution.
375	,,	water.
500	,,	starch-tragacanth paste.
1000		

YELLOW RESIST (INDIGOSOL).

80	grms.	Indigosol yellow I.G.K.
70	,,	Fibrit D.
255	,,	hot water.

Dissolve and add to—

400 grms. starch-tragacanth paste.

Mix well, warm up, cool, and add—

65	grms.	sodium bisulphite 72° Tw.
10	,,	ammonium sulphocyanide.
120	,,	Chrome yellow 60 per cent. paste.
1000		

(3) After printing, the goods are developed in the padding mangle in—

{ 50 grms. Variamine blue salt F.G.
{1000 c.c. water

at a temperature of 77°–86° F., given an air passage of 1–2 minutes, then soured in the open width for ½ minute at 176° F. in—

{ 30 c.c. hydrochloric acid 32° Tw.
{1000 ,, water 176° F.,

then soured again, using half the acid strength, in the rope form, and finally washed and soaped at the boil as usual.

Other Indigosols suitable for the lead chromate process are prepared for printing as under :—

INDIGOSOL-LEAD CHROMATE RESISTS.

	1.	2.	3.	4.	5.
	grms.	grms.	grms.	grms.	grms.
Indigosol Golden Yellow I.G.K.	80	..	..	..	..
,, Green I.B.A.	..	80	..	..	..
,, Pink I.R. Extra	..	..	50	..	..
,, Printing Violet I.B.B.F.	..	..	..	80	..
,, Violet A.Z.B.	..	..	..	..	80
Fibrit D.	70	80	30	30	80
Glycerine	..	..	50	..	..
Solution Salt B.	..	..	30	..	..
Hot water	255	245	235	330	270
Neutral starch-tragacanth thickening	400	400	400	400	400
Sodium bisulphite 71° Tw.	65	..	..	30	..
Potassium sulphite 90° Tw.	..	60	70	..	35
Ammonium sulphocyanide	10	15	15	10	15
Lead chromate paste 60 per cent.	120	120	120	120	120
	1000 grms.				

	6.	7.	8.	9.	10.
	grms.	grms.	grms.	grms.	grms.
Indigosol O. 4 B.	40	..	..	..	..
,, Red Violet I.R.H.	..	80	..	..	..
,, Printing Purple I.R.	..	..	60	..	..
,, Brown I.R.R.D.	..	..	..	40	..
,, Printing Black I.B.	..	..	..	..	15
Fibrit D.	60	50	70	30	..
Glycerine	..	..	..	..	30
Solution Salt B.	..	30	..	30	30
Hot water	330	255	280	350	335
Neutral starch-tragacanth thickening	400	400	400	400	400
Sodium bisulphite 71° Tw.	..	..	60	20	..
Potassium sulphite 90° Tw.	40	55	..	..	60
Ammonium sulphocyanide	10	10	10	10	10
Lead chromate paste 60 per cent.	120	120	120	120	120
	1000 grms.				

(*c*) The *Aluminium Chlorate* process of obtaining Indigosols reserved under Variamine blue is also a non-steaming process, and possesses the further advantage of dispensing with acid oxidation. After the resist colours are printed on naphtholated cloth, in the usual manner, the goods are simply allowed to lie overnight, or better, for 24 hours, exposed to the air. The Indigosols are fully developed during this exposure, and require no further oxidation.

The printing colours for the Aluminium Chlorate process are made up according to the particulars given in the following table:—

Indigosol-Aluminium Chlorate Resists.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol Golden Yellow I.G.K.	40	..	..	..	..	..	..	..	..	..	..
Indigosol Green I.B.A.	..	80	..	..	..	..	..	..	..	..	..
" Green A.B.	..	..	60	..	..	..	..	..	..	..	..
" O. 4 B.	..	..	..	20	..	..	..	..	..	..	..
" Printing Black I.B.	..	..	..	..	20	..	..	..	..	..	..
" Orange H.R.	..	..	..	..	..	60	..	..	..	..	..
" Scarlet H.B.	..	..	..	..	..	..	40	..	..	..	..
" Pink I.R. Extra	..	..	..	..	..	..	..	30	..	..	..
" Printing Purple I.R.	..	..	..	..	..	..	..	..	60	..	..
Indigosol Printing Violet I.B.B.F.	..	..	..	..	..	..	..	..	..	80	..
Indigosol Brown I.R.R.D.	..	..	..	..	..	..	..	..	..	..	20
Glyecine A.	60	60	60	60	50	50	50	50	100	100	50
Solution Salt B.	..	..	50	..	..	50	50	50	..	..	50
Fibrit D.	..	..	..	..	..	50	50	50	..	..	50
Urea	..	..	..	..	..	30	30	30	..	..	..
Warm water	240	200	170	260	270	100	120	130	180	160	170
Neutral starch - tragacanth thickening	500	500	500	500	500	500	500	500	500	500	500
Aluminium sulphate 1 : 1	40	40	40	40	40	40	40	40	40	40	40
Aluminium chlorate 42° Tw.	120	120	120	120	120	120	120	120	120	120	120
	1000 grms.										

After the foregoing resists are printed (on goods prepared with Naphthol A.S.), the cloth is allowed to lie exposed to the air, as already described, until the Indigosols are fully developed. The goods are then developed in Variamine blue according to the usual procedure, and finished off at once by a passage through a cold solution of—

$$\begin{cases} 30 \text{ c.c. sodium bisulphite } 72^\circ \text{ Tw.} \\ 1000 \text{ ,, water,} \end{cases}$$

followed by a thorough wash and a boiling soap treatment.

Although a great variety of fast and fairly bright multicolour combinations may be reserved under Variamine blue grounds by the use of Indigosols alone, it is rarely that they are so used, their chief employment being confined to the production of yellows, greens, and light blues in association with brilliant Azoic reds and oranges.

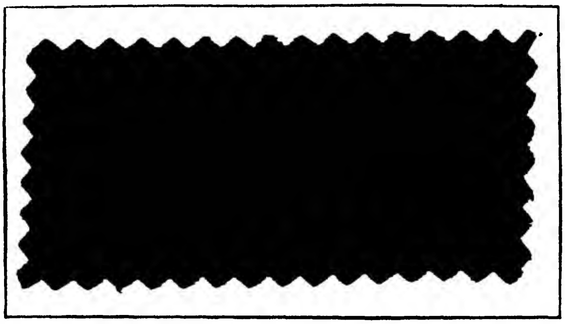
The same may be said of **Indanthrene and other Vat Dyestuffs** in Variamine blue resist styles; they are used only for such shades as cannot be obtained, or

better obtained, from Azoic colours. Details of their application in this connection are given below in the description of Resists under Fast Violet B. base.

Resists under Naphthol A.S./Fast Violet B. Base.

All the methods of producing resist prints under Variamine blue may be applied to grounds of Fast Violet B. Base, or Fast Violet Salt B., without modification ; the two grounds are interchangeable, and are equally well reserved by the same printing colours.

It remains, therefore, only to describe the application of **Indanthrene Resists**, which has been left until now in order to appear along with the illustrative pattern.



(I.G.)

Naphthol A.S./Fast Violet Salt B., resisted { Fast Red Salt T.R. / Indanthrene Brilliant Green 4 G.

(1) Prepare the cloth in—

6	grms.	Naphthol A.S.
20	c.c.	Monopol Brilliant Oil.
10	,,	caustic soda 62° Tw.
To 1000	c.c.	

(2) Dry and print—

RED RESIST.

50	grms.	Fast red salt T.R.
350	,,	water 75°–85° F.
500	,,	starch-tragacanth paste.
100	,,	aluminium sulphate 50 per cent. solution.
1000		

GREEN RESIST.

150	grms.	Indanthrene brilliant green 4 G. double paste fine.
30	,,	Glyecine A.
40	,,	Dissolving Salt B. 1 : 1.
450	,,	British gum paste 1 : 1.
75	,,	carbonate of potash.
100	,,	Rongalite C.
105	,,	water.
50	,,	potassium sulphite 91° Tw.
1000		

(3) Steam for 5 minutes in the rapid ager.

(4) Develop the ground, in the padding machine (fig. 84) omitting steaming box, with—

$\begin{cases} \text{33 grms. Fast violet B. salt.} \\ \text{350 c.c. hot water 75°–85° F.} \end{cases}$

Made up to 1000 c.c.

(5) Sour for ½–1 minute at 140° F., wash and soap as for Variamine blues.

Other Indanthrene or Caledon dyestuffs may be utilised as resists under Variamine blue, Fast violet B. base, or Fast violet salt B. if desired for any particular shade. The two recipes given below represent the general lines on which all such resists are prepared.

INDANTHRENE RESISTS UNDER FAST VIOLET B. BASE OR VARIAMINE BLUE B.

	Blue.	Grey.
Indanthrene brilliant blue 3 G. paste fine	100 grms.	..
,, grey 3 B. double paste fine	..	25 grms.
,, yellow G. ,, ,, ,,	..	2 ,,
Glyecine A.	30 ,,	30 ,,
Dissolving Salt B. 1 : 1	40 ,,	40 ,,
Starch-British gum paste	450 ,,	..
British gum thickening 1 : 1	..	300 ,,
Gum arabic thickening 1 : 1	..	378 ,,
Potassium carbonate	75 ,,	75 ,,
Rongalite C.	100 ,,	100 ,,
Water	155 ,,	..
Potassium sulphite 91° Tw.	50 ,,	50 ,,
	1000	1000

All Variamine blue and Fast violet B. grounds may be developed as well with the diazotised bases as with the specially prepared Fast Colour Salts. The latter are, by far, the more convenient to work, but also the more expensive, and in large scale production the bases are generally preferred. Recipes for their diazotisation and application will be found under "Discharging of Naphthol A.S. Combinations."

On grounds of economy, too, Variamine blue B. base is often replaced by Fast Blue B. base or Fast Blue Salt B. (which are cheaper) for "Red-Blue" styles.

Fast Blue B. base, or dianisidine, yields dark navy blues of good fastness to washing and rubbing, but much inferior to Variamine blue in fastness to light and, therefore, suitable only for goods on which no great demand is made in respect of this last quality.

The process is carried out in much the same manner as with Variamine blue. Thus :—

(1) Prepare in—

$\begin{cases} \text{7·5 grms. Naphthol A.S.} \\ \text{7·5 ,, Naphthol A.S.-B.S.} \\ \text{20 c.c. Monopol Brilliant Oil (or oleine).} \\ \text{22·5 ,, caustic soda 62° Tw.} \end{cases}$

To 1000 c.c.

(2) Dry in the hot flue and print—

RED RESIST.

{30 grms. Fast scarlet R.C. base.
{90 ,, cold water.

Mix to a smooth paste and add—

27 c.c. hydrochloric acid 32° Tw.

Stir into—

500 grms. cold starch-tragacanth paste.

Then add—

{ 10·2 grms. sodium nitrite.
{ 50 c.c. cold water.

Stir the whole for ½ hour and then add—

200 grms. aluminium sulphate 50 per cent. solution.
30 ,, sodium acetate.

To 1000 grms.

(3) Develop in the padding mangle, omitting steaming box (fig. 84), printed side upwards, in the following dye liquor:—

DYE BATH.

{{ 50 grms. Fast blue salt B. (=10 grms. dianisidine).
{{200 ,, tepid water.
{ 260 ,, cold water.
{ 36 ,, potassium persulphate.
{400 ,, water.
40 ,, copper chloride 91° Tw.
10 ,, sodium acetate.

To 1 litre with water.

After developing and airing, the goods are thoroughly sprayed and washed with cold water, then washed at once in hot water, and finally soaped at the boil, washed again, and dried.

Machine Padded Styles with Naphthol A.S., Rapid Fast Colours, and Resists.

Many of the well-known "acid and pad" and "acid and cover" styles, formerly produced by dyeing resisted mordants or by printing steam colours over acid resists, are now much more easily obtained by the use of Naphthol A.S. and Rapid Fast colours. The styles usually consist of a two-colour pattern in white and a dark colour on a plain or finely figured ground of a lighter shade. The plain grounds may either be printed with a pad roller on the printing machine or may be dyed in the customary manner on a padding mangle; the figured grounds are *always printed* with a "cover" roller, engraved with a delicate all-over pattern, such as a fine check, scroll, Bengal lines, honeycomb, etc.

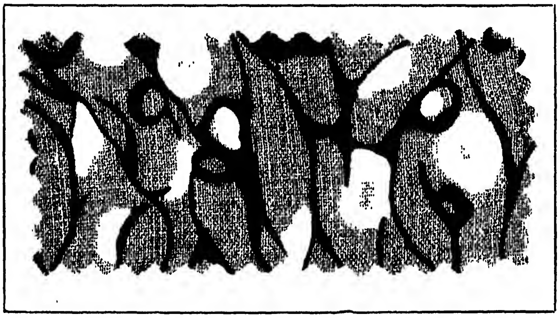
The three patterns shown here were each padded on the printing machine with a plain pad roller; they might, just as readily, have been covered or overprinted with a fine check or close-set line pattern. The method is capable of many modifications, and permits of great latitude in the way both of pattern and colour. Any Azoic colour and a resist may be printed together and subsequently overprinted with any other Azoic colour; and in addition to white

resists, coloured effects may be obtained with Vat or Basic dyestuffs by means of the processes already described.

Process.—The goods, previously prepared with A.S. Naphthols, are first printed with a sulphite or a stannous chloride resist and a Rapid Fast colour, and after drying are then overprinted (*i.e.* padded or covered) with a thickened diazo solution. The Rapid Fast colour is partially fixed by a short steaming in the rapid ager, and the process is completed by passing the goods through a hot dilute solution of acetic acid, followed by a thorough wash and a treatment in boiling soap.

In this manner excellent imitations, in fast colours, of the important and classic " acid red pad pink " Alizarin style are obtainable. The colours are not only of excellent fastness, but are brighter than the Alizarins and possess, in addition, the valuable property of being unaffected by iron salts.

Alizarin Pad Pink Style in Azoic Colours.



(I.G.)

Naphthol A.S.-R.L., printed with White Resist and Rapid Fast Red G.L., and padded with Fast Red R.L. Base.

(1) For this pattern the cloth is slop-padded in—

Prepare.

4	grms.	Naphthol A.S.-R.L.
100	c.c.	oleine 40 per cent.
50	,,	caustic soda 62° Tw.
10	grms.	Nekal B.X. dry.

per 5 litres

(2) Dry and print—

White Resist.

30	grms.	potassium sulphite 91° Tw.
500	,,	neutral starch-tragacanth paste.
470	,,	water (or thickening).
1000		

Red.

150	grms.	Rapid Fast red G.L. paste.
20	,,	Monopol Brilliant Oil.
50	,,	neutral chromate solution (*q.v.*).
280	,,	cold water.
500	,,	neutral starch-tragacanth paste.
1000		

(3) After printing the white and red, dry and print with a pad roller—

PINK.

1 grm.	Fast red R.L. base.
0·5 „	sodium nitrite.
60 c.c.	water.

Mix to a fine paste and stir into—

2 c.c.	hydrochloric acid 32° Tw.
20 „	water.

Allow to stand until dissolved, then stir into—

800 grms. tragacanth thickening 65 : 1000.
1 grm. sodium acetate.

To 1000 grms.

(4) Dry, steam for 3 minutes in the rapid ager at 212° F., pass through a bath of—

10 c.c.	acetic acid 50 per cent.
1000 „	water

at 180° F., wash, soap at the boil, wash, and dry.

If desired, the steaming may be interposed between the first and second printings.

A good stannous chloride resist largely used in practice for all types of Azoic colour resist work, which does not run in steaming and gives, generally, sharper and cleaner cut whites than sulphites, is the following:—

WHITE RESIST S.N.

2400 grms.	British gum (powder).	
750 c.c.	water.	
1200 grms.	glue	soaked and softened before use.
3000 „	water	
450 „	paraffin wax (match wax).	

Boil, cool a little, and add—

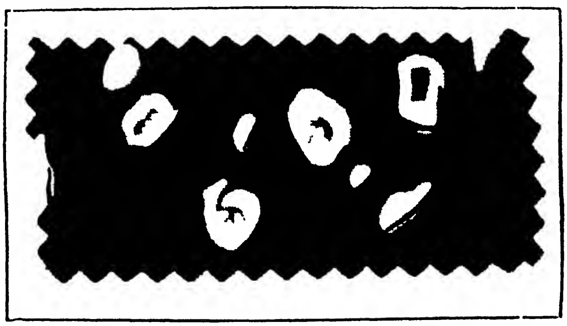
2400 grms. stannous chloride (tin crystals).

Dissolve and add—

450 grms. sodium acetate.

10,650 grms. = 10,000 after boiling.

White resist S.N. is suitable for full red, etc., covers; for lighter covers and pads it must be reduced in strength 1 : 1 or 1 : 2, as required. The reducing paste is prepared as above, omitting stannous chloride and sodium acetate, which are replaced by thickening.



Naphthol A.S. printed with Variamine Blue Salt B. and White Resist, padded with Variamine Blue Salt B. (I.G.).

A great variety of orange, scarlet, bordeaux, brown, blue, and violet colourings may be produced on the same lines as the red and pink above; and if diazo solutions are employed in place of Rapid Fast colours for printing the dark shades, it is

unnecessary to steam the goods. Two examples will suffice to illustrate this method.

(1) PREPARE (pattern on previous page).

Naphthol A.S. 10 grms. per litre.

(2) Dry, and print:—

WHITE RESIST.

As for previous pattern.

DARK BLUE.

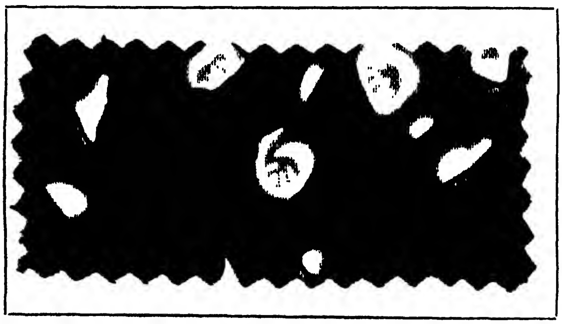
20	grms.	Variamine blue salt B.
10	,,	acetic acid 50 per cent.
470	,,	water.
500	,,	starch-tragacanth paste.
1000		

(3) Dry and pad on the printing machine:—

LIGHT BLUE.

2·5	grms.	Variamine blue salt B.
10	,,	acetic acid 50 per cent.
187·5	,,	water.
800	,,	tragacanth mucilage 65 : 1000.
1000		

(4) Pass through the hot acetic acid bath as for red and pink, wash and soap at the boil with an addition of 2 grms. soda-ash per litre of soap solution, wash, and dry.



White Resist and Fast Violet B. Base printed on Naphthol A.S. and padded Fast Violet B. Base (I.G.).

(1) PREPARE.

Naphthol A.S. 6 grms. per litre.

(2) Dry and print:—

WHITE RESIST.

As previous pattern.

DARK VIOLET.

6·6 grms.	Fast violet B. base.	
40 ,,	hot water.	
2 ,,	sodium nitrite.	

Mix to a fine paste, cool, and stir into :—

400 c.c.	cold water.
7·6 ,,	hydrochloric acid 32° Tw.

Allow to stand ½ hour, filter, and add to—

500 grms.	starch-tragacanth paste.
4 ,,	sodium acetate.

To 1000 grms.

(3) Dry and machine pad with :—

LIGHT VIOLET.

15 parts	Dark violet (above).
50 ,,	tragacanth mucilage 65 : 1000.
2 ,,	acetic acid 50 per cent.

(4) Dry and after-treat exactly as for Variamine blue B.

Another method, the reverse of the foregoing, is occasionally adopted in practice for the production of these padded styles. It amounts to nothing more than the ordinary Rongalite discharge process applied to light dyeings of Azoic colour grounds. A pink ground, for example, may be dyed with a combination of—

Naphthol A.S.-R.L. / Fast red R.L. base
(0·3 grm. per litre) / (1 grm. per litre diazotised),

and after washing, soaping, washing, and drying, the goods printed with a two-colour pattern in—

Rapid Fast red G.L. paste, 150 grms. per kilo.
and a
Rongalite discharge, 100 grms. Rongalite C. per kilo.

After printing, the goods are steamed for 3–4 minutes in the rapid ager at 212° F., developed in acetic acid, and washed and soaped at the boil, exactly as already described for other modes of working.

In *covered* styles, viz. styles in which the ground consists of a fine all-over pattern as distinct from a flat uniform shade, it is customary to print the cover roller in the same dark shade as is used in the first printing ; the amount of white ground showing in the cover pattern (generally 50 per cent. of the area) gives the effect of a lighter shade, and maintains the distinction between pattern and ground. These covered styles are very largely produced in reds and clarets in imitation of the old Madder dyed and Alizarin resist styles, and when executed with selected dyestuffs they are superior in brightness, and much superior in fastness, to their prototypes.

The Rapid Fast and Rapidogen dyestuffs are rarely employed in covered styles. There is no point in using them, since in these styles a single diazo printing colour serves for both pattern and ground rollers, and, moreover, dispenses with the necessity for steaming or special acid developing treatment.

The following combinations yield prints of Indanthrene fastness and give excellent whites when resisted with stannous chloride:—

REDS.

PREPARES.		PRINTING COLOURS.	
Naphthol A.S.	17 grms. per litre.	Fast Red salt 3 G.L.	70 grms. per kilo.
,, A.S.-R.L.	15 ,, ,,	,, R.L. base	10 ,, ,,
,, A.S.-I.T.R.	14 ,, ,,	,, I.T.R. base	16 ,, ,,
,, A.S.-L.T.	14 ,, ,,	,, T.R. base	10 ,, ,,

CLARETS.

Naphthol A.S.-R.L.	12 grms. per litre.	Fast Red B. base,	9 grms. per kilo.
,, A.S.-B.O.	15 ,, ,,	,, ,,	11 ,, ,,

BROWN.

Naphthol A.S.-B.G.	12 grms. per litre.	Fast Scarlet salt G.G.S.	40 grms. per kilo.

Variamine blue B. may be, and is, also used in the same way, but although it is of excellent fastness to washing and light, it is inferior in fastness to chlorine.

The printing colours made up with Fast Colour salts or the diazotised bases, in the proportions given above, are printed along with White Resist S.N. (*ante*) on the appropriate prepares. The goods are dried and reprinted with an all-over " cover " pattern in the same colour, and then finished off by a thorough wash in hot and cold water, followed by a treatment in boiling soap for 20 minutes. The soap solution is made alkaline by the addition of 2 grms. of soda-ash or 5 c.c. silicate of soda, 140° Tw., per litre. After soaping the goods are washed again and dried.

Resists under Nitroso-blue.

The formation of Nitroso-blue, which is produced on the fibre by the condensation of the nitroso bases of tertiary amines with phenols, can be prevented by means of reducing agents like stannous salts and alkali sulphites. On this property is based the process of resisting Nitroso-blue.

The cloth padded in the Nitroso-blue bath is carefully dried in the hot flue and then printed with the resist pastes; steamed for 3 minutes in the rapid ager to develop the blue ground; passed through a solution of tartar emetic to fix the colours, and then washed and soaped.

Tin resists are only suitable for coloured effects, since they give an impure white, due in part to the presence of tannin in the blue padding liquor, and in part to the yellow tinge always given by tin salts to white calico. Sulphite resists, on the other hand, yield a perfect white; but as they do not destroy the tannin, the white is apt to become tinted with blue, from the loose colour removed from the cloth during the washing operations. Nitroso-blue, being in point of fact a Basic colour, is precipitated by tannin, so that if any tannate of antimony is left on the white reserved portions of the cloth, it acts as a mordant for the colour washed out of the ground shade. In many cases the ground shade loses no colour at all in washing, and in such cases a simple sulphite white may be used with success. On the other hand, it is always safer to guard against any possible chance of the white being soiled by adding sufficient caustic soda to the sulphite to destroy effectually the tannin. In this way only can perfect white resists be obtained with certainty.

A fruitful cause of imperfect white resists under Nitroso-blue is to be found in the over-drying of the padded cloth. The drying of these blues is always best carried out in hot-air chambers at as low a temperature as possible; and if properly performed, the cloth ought to be quite a bright yellow colour without a trace of grey. If hot-air machines are not available, cylinder machines may be used; but the first few cylinders must be wrapped with calico, and the rest kept as cool as is consistent with perfect drying. With cylinder drying, a white resist may be printed on the cloth before padding in the blue liquor: this method ensures a better white, since the blue cannot develop on the printed parts however hard the cloth may be dried.

The following recipes are taken from practice, and will serve to illustrate the principles of the Nitroso-blue Resist style:—

NITROSO- OR RESORCIN BLUE PADDING LIQUOR I. (FOR HOT-AIR DRYING).

24	grms.	Nitroso-base M. 50 per cent. (Höchst).
60	,,	warm water.
10	,,	hydrochloric acid 36° Tw.

Dissolve and add—

20	grms.	resorcin.
50	,,	water.
35	,,	tannic acid.
35	,,	water.
70	,,	10 per cent. solution oxalic acid.
50	,,	6 per cent. tragacanth thickening.
396	,,	water.

Mix well, and before use stir in for some time—

10	grms.	phosphate of soda.
240	,,	water. Make up to—
1 litre		

NITROSO-BLUE PADDING LIQUOR II. (FOR CYLINDER DRYING).

25	grms.	Nitroso-base M. 50 per cent. paste.
30	,,	ortho-phosphoric acid 50 per cent.
75	,,	warm water.
20	,,	resorcin.
50	,,	water.
50	,,	tannic acid.
200	,,	water.
5	,,	oxalic acid.
200	,,	water.
50	,,	6 per cent. tragacanth thickening. Make up with water to—
1 litre		

Pad the white cloth in either of the above solutions, dry gently, and print on any of the following resists:—

White Resist I.

250 grms. British gum (powder).
750 „ potassium sulphite 90° Tw.

1000

Heat to 70° C. and cool.

White Resist II.

225 grms. British gum (powder).
600 „ potassium sulphite 90° Tw.
175 „ caustic soda 90° Tw.

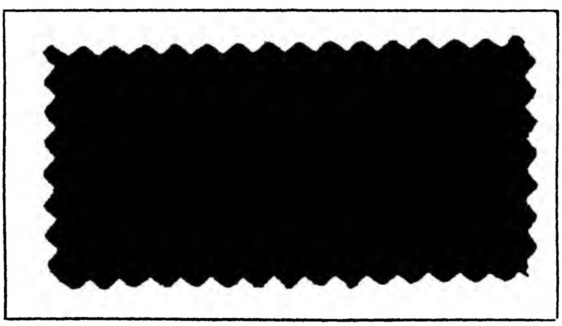
1000

Heat to 70° C. and cool.

White Resist II. is the more generally useful. Coloured resists are made from Basic colours; they contain no tannin, as there is sufficient for their fixation in the blue padding liquor. The resisting agent may be either stannous chloride or potassium sulphite.

Tin Resists.

	Red N.	Pink N.	Yellow N.	Green N.	Blue N.
Auramine O.	5	..	30	20	..
Rhodamine 6 G. extra	25	10	..	..	..
New methylene blue N.	..	..	..	..	10
Brilliant green cryst. extra	..	..	..	10	..
Acetic acid	200	200	200	200	200
Citric acid	25	25	25	25	25
Water	355	355	355	355	375
Starch	90	90	90	90	90
6 per cent. tragacanth	150	170	150	150	150
Acetin	50	50	50	50	45
Boil, cool, and add—					
Stannous chloride	50	60	50	50	55
Acetate of soda	50	40	50	50	50
	1000	1000	1000	1000	1000



Tin Resists under Nitroso-blue (I.G.).

For this pattern the cloth was prepared in Nitroso-blue Padding Liquor I., dried in the hot flue, and printed with :—

Resist Blue.

30	grms.	Methylene blue D.R.
125	,,	acetic acid 9° Tw.
200	,,	water.
50	,,	Acetin N.

Dissolve and add—

495	grms.	tragacanth mucilage 60 : 1000.
50	,,	"tin crystals" ($SnCl_2$).
50	,,	sodium acetate.
1000		

Orange Resist.

As Blue above, but with 25 grms. Flavophosphine R. conc. new per kilo.

After printing, steam for 3 minutes in the rapid ager, wash and soap in the open soaping range, wash, and dry.

The following coloured resists are based upon the process published by Messrs. Meister, Lucius & Brüning, the patentees of Nitroso-blue. They give bright, fast colours, and a sharp, clear-cut impression of the engraving. In composition they consist essentially of Basic colouring matter, thickening, and sulphite of potassium. The addition of antimony salts is not absolutely necessary, but it adds to the fastness and brightness of the colours, and is therefore an advantage.

Coloured Sulphite Resists B.S.

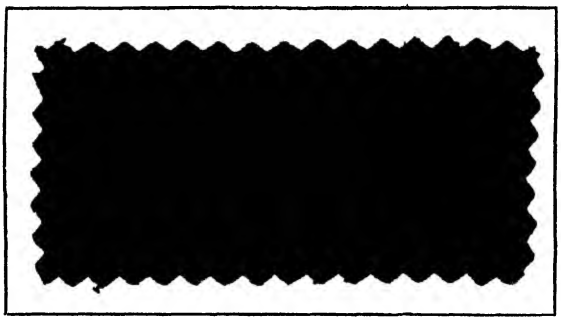
	Red.	Pink.	Yellow.	Blue.	Green.	Olive.
Auramine O.	5	..	30	..	20	23
Rhodamine 6 G. extra	25	15	..	..	..	1
Malachite green cryst.	..	..	..	..	10	..
New methylene blue N.	..	..	..	10	..	6
Water	200	215	200	220	200	200
Glycerin	30	30	30	30	30	30
Thickening A.T.	590	590	590	590	590	590
Potassium sulphite 90° Tw.	150	150	150	150	150	150
	1000	1000	1000	1000	1000	1000

Violet = mixtures of pink and blue.
Brown = ,, red, yellow, and a little blue.
Orange = ,, red and yellow.

Thickening A.T. (for above).

40	grms.	Antimonin.
300	,,	water.
50	,,	starch.
200	,,	6 per cent. tragacanth thickening.
590		Boil and cool.

After printing sulphite resists on cloth padded in Blue liquor I. or II., the goods are dried, and steamed for 3 minutes in the rapid ager at 100° C.; then passed through a tartar emetic bath, and finally washed and soaped.



Sulphite Resists under Nitroso-blue (I.G.).

The pattern illustrated was produced by printing the following sulphite resists on cloth prepared in Nitroso-blue Liquor I.:—

RESIST COLOURS.

	Red.	Green.
Auramine O.	5·5 grms.	15 grms.
Safranine O.	16 ,,	..
Rhodamine 4 G.	32 ,,	..
Malachite green crys. extra	..	15 ,,
Water	290 ,,	320 ,,
Glycerine	30 ,,	30 ,,
Antimony thickening (below)	500 ,,	500 ,,
Potassium sulphite 90° Tw.	120 ,,	120 ,,
Make up to	1000	1000

ANTIMONY THICKENING.

40 grms.	wheat starch.
300 ,,	British gum, dry.
335 ,,	water.
250 ,,	tragacanth mucilage 60 : 1000.
75 ,,	Antimonin (lactate).
1000	

After printing, steam, wash, and soap as for tin resists.

Resists Printed before Padding.—For obtaining white effects by printing on plain cloth before padding in Nitroso-blue, either of the two following resists is suitable. Both yield a good white, and both withstand the run through the blue padding liquor, and drying over steam-heated cylinders.

RESIST WHITE III. (TIN RESIST).

$\left\{\begin{array}{l}\text{55 grms. glue.}\\ \text{180 ,, water.}\end{array}\right.$

Allow to soak until the glue is quite soft and then add—

200 grms.	British gum.
305 ,,	water.
30 ,,	acetic acid 50 per cent.
70 ,,	sodium tartar emetic. Boil, cool, and add—
120 ,,	stannous chloride.
40 ,,	acetate of soda.
1000	

Resist White IV. (Sulphite Resist).

150 grms. China clay paste 50 per cent.
170 ,, water.
90 ,, starch.
220 ,, gum Senegal 50 per cent. solution.

Boil, turn off steam, and whilst hot add—

20 grms. white wax } previously dissolved.
75 ,, turpentine }

Mix well in, cool, and add—

275 grms. potassium sulphite 90° Tw.

1000

Print on plain white cloth ; dry well, and then pad in Nitroso-blue II. in a mangle similar to that used for Azoic colour resists ; dry at once, but not too hard, over a cylinder drying machine, the first four cylinders of which are wrapped with calico. Then steam for 3 minutes in the rapid ager at 100° C. ; pass through a solution of tartar emetic ; wash well, soap, wash, and dry.

The Nitroso-blue style finds its chief application in the production of flannelette goods, and especially of those in which the printed pattern is raised through to the back of the material.

Aniline Black Resist Styles.

The introduction by Lightfoot, in 1863, of a practical method of printing Aniline black, almost immediately suggested to calico printers the desirability of producing white and coloured effects under printed covers and pads of so important and fast a colour. The first experiments in this direction were based upon the fact that Aniline black is an oxidation product ; hence the earliest resists consisted of reducing agents. Later on it was ascertained that the presence of a mineral acid, either free or produced in steaming or ageing, by the dissociation of an unstable salt, was quite as essential as the presence of an oxidising agent to the development of the black. Alkaline salts and other neutralising substances, therefore, were employed, either as such or in combination with reducing agents, to prevent the formation of Aniline black in certain parts of the cloth. By printing patterns in colours containing sulphocyanides, xanthates, thiosulphate of soda, tannin, sodium carbonate, chalk, etc., many excellent results were obtained ; but it was not until Prud'homme brought out his well-known process that the Aniline Black Resist Style became popular in the calico-printing industry. Up to that time it had only been possible to dye the cloth on one side, and that by means of printing with a pad roller. The goods were first printed with a resist, then dried, and padded with thin Aniline black paste on the printing machine. In Prud'homme's process, however, the second printing is dispensed with, the cloth being dyed by passing through a solution of aniline, containing all the ingredients necessary to the formation of Aniline black when the cloth is subsequently steamed. In this way the material is dyed uniformly on both sides, and has a much richer appearance than when the black ground is printed by machine.

Although all patterns on Aniline black grounds, except those produced by direct blotch printing, are obtained by means of resist pastes of one sort or another, they are classed in two different categories according to their mode of execution. If the resist pastes are printed on the cloth before the black padding liquor is applied to it, the effects so obtained are known as *resists* ; if, on the contrary, the cloth is padded with the black liquor before the resists are printed, they are known in the trade as *discharges*. Properly speaking, they are not discharges at all, for the black is only developed by steaming *after*

the resists have been printed, and is not developed on the printed parts; but the term, discharge, is useful to distinguish between the two methods.

The resist and the discharge processes both have their advantages and disadvantages. In the first, pure whites and bright colours are almost always obtained without the slightest difficulty, but the impression of the pattern is often lacking in sharpness. On the other hand, a crisp definition of the design, with clear-cut edges, is characteristic of the discharge process; but unless the utmost care is exercised at every step in its application, the whites and colours are very liable to become dull and dirty in appearance. In spite of its greater difficulty, however, the discharge process is usually preferred for high-class work, because, when employed under favourable conditions, it yields colour effects of greater depth, richness, fastness, and variety than can be obtained from the resist process.

Prud'homme Aniline Black Resist Styles.

Prud'homme's original process is still in use at the present time, but many improvements and some modifications of it have been introduced by various chemists and practical calico printers, most of the improvements having been effected in the direction of applying new colouring matters and different resisting agents.

Briefly described, the process is as follows:—The white bleached cloth is first padded in Prussiate black (Aniline hydrochloride, chlorate of soda, and potassium ferrocyanide); it is then gently dried, care being taken not to oxidise the Aniline, and printed with the resist pastes, dried, and steamed 3–4 minutes in the rapid ager to develop the black ground and to fix the reserve colours; finally, it is chromed, washed, soaped, and dried. This method of working constitutes the discharge method so called.

The resist method is almost identical with the above, except that the resists are printed on plain white cloth, well dried, and sometimes steamed, then padded in the black liquor, dried again, steamed 3–4 minutes, chromed, washed, and soaped.

Colours for the discharge process may either contain, or be entirely free from, insoluble plastic bodies, but those for the resist process only give good results when they contain insoluble resisting agents such as zinc oxide, chalk, etc.

The most commonly used resisting agents are zinc oxide, zinc acetate, sodium acetate, magnesium acetate (all of which neutralise the acidity of the black), and sulphite of potash and sulphocyanide of potash, which act as reducing agents.

For coloured resists, a good many colouring matters are available; but, with the exception of Basic colours, Pigment colours, and Direct colours, very few find any extensive application in practice. The alkalinity of the vat dyestuff printing pastes has been utilised with success in special styles, and the Sulphur colours are also occasionally employed for faster classes of work. On the whole, however, the Basic colours give the finest and largest range of colours; and being miscible in any proportions, they are consequently the most useful, since they yield both brilliant and subdued tints, and dark, full shades. The Pigment colours are used mainly for yellows and oranges in goods for the foreign markets; and the Direct colours are employed solely for crimps —a style requiring the colours to withstand the action of strong caustic soda solutions.

Some years ago Pluzanski succeeded in perfecting a process for producing Azoic colour resists under Aniline black; his process, though yielding excellent results under both covers and dyed blacks, has not become general, having been superseded by more convenient methods.

Numerous formulæ have been suggested and employed for resisting Aniline black; but they are all founded on the same principles, and no good purpose would be served by enumerating them. In the following descriptions of the more important methods of resisting Aniline black, the recipes are taken, for the most part, from actual practice, or from the results of bulk trials; and where this is not the case, they are quoted from the published articles of those who have had experience of their practical working. The same remarks apply equally to the handling of the goods, so that, on the whole, the processes given below may be taken as representing not merely concrete, but also typical, examples of the means and methods in current use.

Discharge Styles on Aniline Black.

In this process, as already mentioned, the cloth is padded in Aniline black liquor before the colours are printed upon it. The condition of the cloth after padding and drying is perhaps the most important factor in determining the purity of the white and the brilliancy of the colours in the finished print.

In order to secure the best results, the following precautions must be observed:—

(1) The discharge pastes must be printed on cloth on which the black is unoxidised. This is absolutely essential, and can only be ensured by using a freshly prepared black solution, and by drying the cloth at as low a temperature as the speed of the drying apparatus will allow. Aniline black liquors which have stood for some time become partly oxidised and impart a greenish colour to the cloth. The same effect is also produced by drying at too high a temperature. In either case dirty whites and flat colours are the result. On emerging from the drying machine the goods ought to be of a light yellow tint without a trace of green. If they are at all green they are unsuitable for light-coloured effects, and must be utilised if possible for the printing of opaque pigment yellows, oranges, or greens.

(2) After drying, the padded goods are cooled at once to prevent the oxidation of the aniline, and are then printed as soon as possible. In the warm atmosphere of a printworks, the black develops very rapidly, especially if the pieces are warm.

(3) Over-drying after printing must be carefully avoided, since the richness and beauty of the black is impoverished thereby.

(4) The printed goods must be steamed immediately after printing, and before the cloth has become a dark green shade. The steam must be at 90°–95° C. and ought not to be too moist, otherwise the colours are apt to run, and the whites invariably become yellowish.

(5) The whole process, from start to finish, must be carried out without any considerable interval being allowed to elapse between the various operations. This applies in an equal degree to the washing and chroming, etc., which should be proceeded with as soon as convenient after the goods are steamed.

Process:—Pad the cloth in Black P. or Black P.S.

Black P.

I.	75	grms.	aniline salt.
	200	,,	water.
II.	35	,,	chlorate of soda.
	400	,,	water.
III.	40	,,	yellow prussiate of potash.
	250	,,	water.
	1000		

Mix I., II., and III. immediately before use. Black P. is useful for heavy goods and ordinary mercerised goods; for the latter it may even be diluted somewhat (3 parts black, 1 part of water), and still give a full shade.

BLACK P.S.

I.	85	grms.	aniline salt.
	150	„	water.
	50	„	6 per cent. tragacanth thickening.
II.	39	„	chlorate of soda.
	300	„	water.
III.	45·5	„	yellow prussiate of potash.
	330·5	„	water.
	1000		

Mix I., II., and III. in the cold, and make to 1 litre before use. Black P.S. is employed when a denser black is wanted; for most purposes, however, the weaker and cheaper Black P. is sufficiently dark.

After padding, which is done in any of the ordinary types of padding machine, the goods are carefully dried, and then printed with any of the resists or discharges given below.

PIGMENT DISCHARGES.—Pigment and lake colours are fixed by albumen. The resisting agents employed are either soda-ash or acetate of soda.

	YELLOW P.	ORANGE P.	RED P.	BLUE P.	GREEN P.
Chrome yellow paste	400	..	..	..	..
„ orange „	..	350	..	..	..
„ lemon „	..	..	..	..	150
Ultramarine blue	..	..	..	330	..
Guignet's green	..	..	..	..	200
Vermilion	..	..	200	..	..
Glycerin	..	..	..	30	30
Water	..	..	250	105	..
Soda ash	75	75	75	75	..
Acetate of soda	..	..	..	..	200
Gum tragacanth 6 per cent.	325	375	200	110	200
Albumen solution 50 per cent.	200	200	250	350	200
Turpentine	..	..	25	..	20
	1000	1000	1000	1000	1000

Grind the ingredients together in a mill before use. Print on black padded cloth; steam 3–4 minutes in the rapid ager; pass through a ½ per cent. solution of bichromate of soda at 50°–60° C., wash well, soap, wash, and dry.

ZINC OXIDE DISCHARGES.—In these discharges, the colouring matters employed are the Basic colours. Their fixation is effected by the zinc ferrocyanide formed by double decomposition during the steaming. The zinc oxide process was worked out and patented by W. E. Kay at the Thornliebank Printworks, and yields very bright and fairly fast colours, especially when magnesium acetate is used along with the zinc oxide. The addition of albumen increases the fastness of the colours, and their brilliancy is further increased by padding the cloth in Turkey-red oil previous to passing it through the black bath. Excess of oil must be avoided, otherwise the development of the black is retarded. In practice, a solution of ammonia-oleine (sulphoricinoleate of ammonia), corresponding to 1¼ per cent. of fatty acid, is used with success in

conjunction with either Black P. or Black P.S. Pad the cloth in the oil, dry over cylinders, cool, and pass through the black bath, dry in hot air, and print on the discharges. Then steam, etc., as above.

The best whites are produced by a mixture of potassium sulphite, sodium bisulphite, and acetate of soda. Light colours are improved also by the addition of the same mixture to the paste used for reducing them to shade. For dark colours zinc oxide and magnesium acetate give satisfactory results, without any further addition of other resisting agents.

In all zinc oxide resist colours it is advantageous to add a little albumen for the purpose of rendering them more resistant to the action of soap. Soaping increases the beauty of the black, the brightness of the colours and white, and in many cases is necessary if only to get the cloth into fit condition for finishing. Hence, if the balance of the colour scheme is to be preserved, each colour must be fairly fast to soaping.

In this respect the following colours can be recommended: they give very bright and transparent shades, of excellent fastness to washing and soaping, especially when printed on oiled cloth, and they possess the further merit of having withstood the test of many years' practical application on the large scale.

Basic Colour Discharges (Zinc Oxide and Magnesium Acetate).

	Red.	Pink.	Gold.	Yellow.	Green.	Blue.	Navy.	Purple.
Rhodamine 6 G. extra	23	10	0·5	..	..	..	..	..
Rhodamine B. extra	..	2	..	..	..	..	..	..
Auramine O.	2	..	20	..	..	..	..	..
Acridine yellow G..	..	..	..	20	22	..	..	..
New solid green 2 B.	..	..	..	..	10	..	..	..
Thionine blue G.O.	..	..	..	..	..	20	..	..
Marine blue S.	..	..	..	..	..	..	20	..
Methyl violet B. extra	..	..	..	..	..	..	..	20
Glycerin	30	20	30	30	30	30	30	30
Water	150	133	114·5	115	110	115	115	115
Dissolve, and add—								
Cold water	..	35	35	35	30	35	35	35
6 per cent. tragacanth thickening	95	100	100	100	98	100	100	100
Discharge paste A.	600	600	600	600	600	600	600	600
Mix well in, and add—								
Albumen solution 50 per cent.	100	100	100	100	100	100	100	100
	1000	1000	1000	1000	1000	1000	1000	1000

Orange = { 1 part red.
3 parts gold.

Olive 1.6.2. = { 1 part pink.
6 parts yellow.
2 ,, blue.

Brown 8.24.1 = { 8 parts pink.
24 ,, yellow.
1 part blue.

Peacock blue = { 1 ,, green.
3 parts blue.

Grey shades are difficult to mix from Basic colours, for reasons already dwelt upon in the section on Compound Shades; they are usually made, therefore, from pigments. Thus—

Grey :—	140	grms.	Ultramarine blue (powder).
	70	,,	lampblack (powder).
	490	,,	6 per cent. tragacanth. Grind together, and add—
	200	,,	50 per cent. albumen solution.
	200	,,	acetate of soda.
	1 litre.		Grind the whole before use.

Discharge Paste A. (for Basic Discharge).

100 grms. zinc oxide.
150 ,, magnesium acetate.
250 ,, 6 per cent. tragacanth thickening.
100 ,, starch paste.

600

Reducing Paste (for Light Shades).

700 grms. Discharge paste A.
250 ,, White discharge B.
50 ,, 40 per cent. egg albumen solution.

1000

White Discharge B.

100 grms. starch.
60 ,, British gum.
300 ,, potassium sulphite 90° Tw.
288 ,, water. Boil and add—
150 ,, sodium acetate. Cool and add—
100 ,, bisulphite of soda 66° Tw.
2 ,, Ultramarine blue (for sightening).

1000

The above paste gives an exceedingly pure white on freshly padded cloth. If the cloth has become slightly green, a good white can still be obtained by printing Resist B.N.F., which contains a little hydrosulphite.

Resist White B.N.F.

385 grms. starch paste.
385 ,, 6 per cent. tragacanth thickening.
30 ,, Hydrosulphite N.F. conc.

Heat to 60°–70° C. to dissolve the hydrosulphite, cool, and add—

200 grms. acetate of soda.

1000

The above colours and white discharges are printed on cloth prepared as follows :—

1*st*. Pad in :— 100 grms. ammonia Turkey-red oil 25 per cent.
1900 ,, water.

2000 = 1¼ per cent. fatty acid.

2*nd*. Dry and pad in either Black P. or Black P.S. ; dry gently, so that the cloth leaves the drying machine with a light yellow tint only.

After printing, the goods are dried carefully and steamed at 90° C. for 2–3 minutes in the rapid ager. They are then passed in the open width through a lukewarm chrome bath (5 grms. bichromate of soda per 1000 grms. water), washed well, soaped lightly at 60° C., washed, and dried.

Coloured discharges may also be obtained with zinc acetate instead of the foregoing, but they are neither so bright nor so fast.

COLOURED DISCHARGE WITH ZINC ACETATE.

20	grms.	Basic dyestuff.
200	,,	water.
50	,,	acetic acid.

Dissolve, and add—

280	grms.	6 per cent. tragacanth thickening.
300	,,	starch paste.
150	,,	zinc acetate in crystals.
1000		

Zinc acetate prevents the development of the black during steaming and, by double decomposition with the yellow prussiate, forms zinc ferrocyanide, which fixes the basic colour. Albumen has been recommended as an addition to zinc acetate resists, but its use is somewhat irrational, since soluble zinc salts have a tendency to coagulate the albumen in the printing paste.

Zinc oxide alone gives very bright resist effects, but the colours have the appearance of pigments, owing to the large amount of solid matter they contain. In some styles this is an advantage, whereas for sateens and flannelettes the more transparent the colour the better.

Generally speaking, the zinc oxide content of colours for these latter classes of work ought not to exceed 10 per cent.

BROWNING'S PROCESS.—As tannate of antimony is the best mordant for basic colours, many attempts were made to apply it in the Aniline black resist styles. The earlier experiments, which consisted in adding various reserving agents to mixtures of Basic colour and tannin, gave very inferior results, and the problem was left unsolved until Browning, of the Broadoak Printworks, Accrington, introduced his patented process. This consisted in padding cloth, mordanted in the usual way (as for dyeing) with tannic acid and tartar emetic, in a Prussiate black, drying as usual, and then printing on a thickened mixture of Basic colour solution and acetate of soda, followed by steaming, chroming, and washing. Acetate of magnesium and acetate of zinc may also be used as resists, and are indeed to be preferred, as the hydrates exercise little or no injurious influence on the Basic colours. Acetate of soda, on the contrary, if used in excess, is apt to yield bad results with some of the Basic colours, especially if they be delicate in shade.

Acetate of soda discharges contain from 15–20 per cent. by weight of acetate of soda, according to the depth of the engraving.

During steaming, the Basic colour combines with the tannate of antimony to form an insoluble lake, while the metallic acetates prevent the development of the black on the printed parts of the cloth. White effects are best obtained by means of a strongly alkaline sulphite or acetate paste, which destroys the tannate of antimony on the cloth, but in many cases, such, for instance, as superposition effects of colour on white, this is inapplicable, and must be replaced by the ordinary acetates of soda, zinc, or magnesium, or the sulphite of potash pastes. Although, under proper conditions, these give sufficiently good whites, they cannot compare with the white obtained by Prud'homme's method for purity.

The following is a résumé of the Browning process :—

(1) Pad the cloth in—

$$\begin{cases} 12{\cdot}5 \text{ grms. tannic acid.} \\ 1000 \quad ,, \quad \text{water. Dry.} \end{cases}$$

(2) Fix the tannin by a run through—

$$\left.\begin{cases} 10 \text{ grms. tartar emetic} \\ 5 \quad ,, \quad \text{chalk} \\ 1000 \quad ,, \quad \text{water} \end{cases}\right\} \text{at } 30^\circ\text{–}40^\circ \text{ C.}$$

Well wash in water.

(3) Open soap at 75°–80° C. in a neutral soap bath containing 2½ grms. soap per litre. Wash well and dry. Soaping, curious though it may appear, is one of the most important operations in the process. Experience has shown beyond doubt that good whites, good colours, and a full, rich black cannot be obtained unless the tannin-mordanted goods are soaped, and thoroughly well washed afterwards.

(4) Slop-pad in any type of mangle padding machine with Black P. or P.S. Dry as usual for Aniline black resist styles and then—

(5) Print on the discharge colours given below.

(6) Dry and steam for 2–4 minutes in the rapid ager at 85°–90° C.

(7) Chrome in a ½ per cent. solution of bichromate of soda at 30° C. Wash well, soap lightly, wash, and dry.

The whites and colours are prepared according to the following directions :—

White Discharges.

	1	2	3	4	5
Zinc oxide 50 per cent. paste	200	..	..	..	..
Starch paste 12 per cent.	398	..	..	298	398
Tragacanth 6 per cent.	250	..	..	425	225
British gum	..	80	200	..	..
Water	..	288	178	..	..
Caustic soda 90° Tw.	..	..	120	..	..
Sulphite of potash 90° Tw.	..	300	500	..	..
Bisulphite of soda 66° Tw.	..	100	..	..	125
Hydrosulphite N.F. conc.	..	..	..	25	..
Ultramarine blue	2	2	2	2	2
Acetate of soda	150	150	..	250	250
Starch	..	80	..	..	..
	1000	1000	1000	1000	1000

Nos. 1, 2, 4, and 5 are suitable for most classes of work ; No. 3 for styles in which large white objects appear, or which have no superposition effects over or under the white. All five are strong enough for the finest patterns.

The coloured discharges may be made up from either sodium, zinc, or magnesium acetate. The two last give the brightest colours taken altogether, and zinc acetate gives the fastest, by reason of the fact that an additional mordant is introduced by the formation of ferrocyanide of zinc. In preparing the printing pastes, the Basic colour is first dissolved in suitable solvents, and then added to a mixture of water and British gum ; the whole is then heated

to dissolve the gum, and when the paste is perfectly smooth it is cooled down to about 30° C., at which temperature the zinc and sodium acetates are added. They dissolve readily in the lukewarm paste without any assistance other than an occasional stirring up. With magnesium acetate, which is most conveniently prepared in solution, the procedure is somewhat different. The dyestuff solution, together with a little thickening, is added lukewarm to a thickened solution of the acetate previously prepared, and kept as a stock paste.

BASIC COLOUR DISCHARGES FOR BROWNING'S PROCESS (ACETATE OF SODA).

	RED.	PINK.	ORANGE.	YELLOW.	GREEN.	BLUE.	VIOLET.
Rhodamine 6 G. extra	23	15	7·5	..	..	..	..
Auramine O.	2	..	22·5	20	..	..	..
Acridine yellow G.	..	..	..	..	8	..	..
New solid green 2 B.	..	..	..	..	16	..	..
Methyl violet B. extra	..	..	..	..	..	..	20
Thionine blue G.O.	..	..	..	..	..	20	..
Water	305	310	300	310	326	310	310
Acetic acid 9° Tw.	150	155	150	150	150	150	150
Glycerin	50	50	50	50	50	50	50
Methylated spirits	20	20	20	20	..	20	20
British gum	200	200	200	200	200	200	200
Heat, and cool to 30° C., and add—							
Acetate of soda	250	250	250	250	250	250	250
	1000	1000	1000	1000	1000	1000	1000

For a Dark royal blue replace Thionine blue by Marine blue.
,, Bluish green use Solid green 2 B. without any yellow.
,, Brown take { 14 grms. Auramine O; 4 ,, Methyl violet B. extra; 5 ,, Rhodamine 6 G. extra } per kilo. of colour as above.
,, Reddish purple { 16 ,, Methyl violet 6 R.; 4 ,, ,, ,, B. extra } per kilo. of colour.

Olives and various other compound shades may be made in a similar manner from suitable mixtures of blue, yellow, and pink.

BASIC COLOUR DISCHARGES FOR BROWNING'S PROCESS (ACETATE OF ZINC).

Instead of 250 grms. of acetate of soda use 150 grms. of zinc acetate (crystals). Thus—

20–25	grms.	Basic colour.
310–305	,,	water.
150	,,	acetic acid 9° Tw.
50	,,	glycerine.
20	,,	methylated spirits.
200	,,	British gum. Heat and cool, then add—
150	,,	zinc acetate.
100	,,	water or gum solution.
1000		

Basic Colour Discharges (Magnesium Acetate).

Type:—

20–30	grms.	Basic dyestuff.
205–195	,,	water.
100	,,	acetic acid 9° Tw.
25	,,	methylated spirit.
50	,,	glycerine.
100	,,	British gum. Dissolve, cool, and add—
500	,,	magnesium acetate thickening.
1000		

Magnesium Acetate Thickening.

400	grms.	magnesium acetate 40° Tw.
100	,,	British gum.
500		

The magnesium acetate is prepared by saturating acetic acid with magnesium carbonate:—

1000	grms.	magnesium carbonate.
3000	,,	acetic acid 12° Tw.
4000		

Add a slight excess of the carbonate, and when no more carbonic acid is evolved heat the solution gently until the filtered liquor contains no more iron, which is always present in commercial carbonate of magnesium; then allow to settle, decant the supernatant liquor, and neutralise with acetic acid. Set at 40° Tw.

The printing, steaming, etc., of the three foregoing classes of discharge colours are identical in every respect.

The colours produced by Browning's method have the advantage of containing no insoluble matter, neither do they impart any stiffness to the cloth, nor fill up the fibre like the zinc oxide resists. They possess a beautiful quality of transparency, and are unsurpassed for softness of effect. In brightness, however, they fall far behind the zinc oxide colours; and as the latter also yield subdued effects, with a considerable amount of transparency, they have practically displaced the acetate basic colour discharges on antimony tannate.

Apart from all questions of artistic value, the Browning process is too expensive and slow to compete with the zinc oxide process, which, when properly handled, leaves little to be desired in the way of either brightness, softness, transparency, or fastness of the colours, and which, as regards the purity of the whites, is superior.

For flannelettes and certain sateen goods, in which a maximum softness of the cloth is essential to the attainment of the best results, and for rich effects of dark colours on cotton velvet, the Browning process is still used to a limited extent; for all other styles it has been discarded by most printers.

With a view to shortening the process, the direct addition of tannin to the black padding liquor has been suggested. Such an addition certainly does away with the six operations of tanning, drying, fixing, drying, soaping, and drying, that the cloth is put through before padding black, but it is open to several objections, and is at most only a poor substitute for the previous mordanting of the cloth. In the first place, not more than 2½ grms. of tannic acid per litre of black solution can be used without affecting the beauty and fullness

of the ultimate black ; secondly, this quantity of tannin is insufficient properly to fix even medium shades of Basic colours; and thirdly, the colours themselves are neither so bright, nor so fast, nor so intense as those obtained by means of the original and more rational process.

THE KATANOL PROCESS.—This process represents the latest development in the production of Basic colour reserves on Aniline black grounds. In principle it resembles the Browning process, but is shorter and simpler, no preliminary fixing or soaping operations being necessary before the goods are padded in Aniline black. Katanol, which as already described acts as a mordant for Basic dyestuffs, has a strong affinity for the fibre and is sufficiently fixed thereon by the simple process of drying, and still more so by the subsequent passage through the acid Aniline black padding liquor, which precipitates it in an insoluble form.

Process.—Pad the goods in a two-bowl mangle through a solution of:—

12	grms.	Katanol O.N.
1·2	,,	soda-ash.
10	,,	Monopol Brilliant Oil.
To 1 litre		

Dry and re-pad in the following Aniline black liquor:—

ANILINE BLACK LIQUOR:—

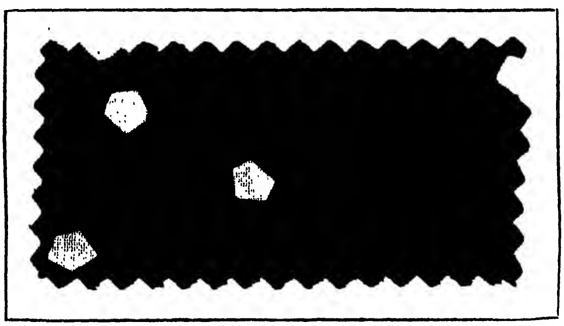
(1)	80	grms.	aniline salt.
	300	,,	water.
(2)	54	,,	yellow prussiate of potash.
	200	,,	water.
(3)	30	,,	sodium chlorate.
	200	,,	water.

Mix (1), (2), and (3), and before use add—

5 grms. formic acid 90 per cent.

To 1 litre

Dry gently in hot air and print the reserves given below.



White and Basic Blue reserved under Aniline Black.
Katanol Process (I.G.).

WHITE RESERVE.

100	grms.	Lithopone (red seal brand).
50	,,	magnesium oxide.
200	,,	gum arabic 1 : 1.
650	,,	potassium sulphite 90° Tw.
1000		

Blue Reserve.

20	grms.	Methylene blue D.B.B.
20	,,	phenol.
70	,,	methylated spirit.
25	,,	Acetin N.
65	,,	water.

Dissolve and add to:

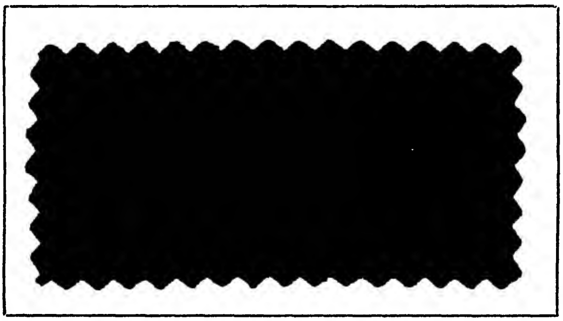
800 grms. Reserve thickening K. (below).

1000

Reserve Thickening K.

700	grms.	British gum 1 : 1.
80	,,	Lithopone.
40	,,	sodium acetate.
45	,,	potassium sulphite 90° Tw.
50	,,	glycerine.
20	,,	castor oil.

Make up to 1000 grms. with water.



Basic Colour Reserves under Aniline Black-Katanol (I.G.).

Colour Reserves:—

	Pink.	Green.
Astrophloxine F.F. extra	30 grms.	..
Auracine G.	..	20 grms.
Rhoduline pure blue 3 G.	..	20 ,,
Phenol	20 ,,	20 ,,
Methylated spirit	70 ,,	70 ,,
Acetin N.	25 ,,	25 ,,
Water	55 ,,	45 ,,
Reserve thickening K.	800 ,,	800 ,,
	1000	1000

After printing and drying, the goods are steamed for 4 minutes in the rapid ager at 212° F., passed through a warm bath of—

1 grm. bichromate of potash.
5 grms. soda-ash.

To 1000 c.c. with water

at 100°–105° F., well washed and lightly soaped, washed, and dried. Chroming, washing, and soaping may be carried out in the open soaper.

Any other Basic dyestuff capable of withstanding potassium sulphite may be used as a coloured reserve.

Resists on a Katanol base possess better fastness to washing than those on tannate of antimony, and are quite as bright.

NAPHTHOL A.S. RESISTS ON PADDED ANILINE BLACK.—Strongly alkaline solutions of A.S. Naphthols when printed on Aniline black pads, and subsequently developed in diazo-solutions, yield yellow, orange and red resists of great brilliancy and of exceptional fastness. Violet and blue resists may also be obtained in the same way, but only in combination with white or a brownish-yellow of little interest, as no blue or violet base gives a pure yellow, orange, or red shade with any naphthol.

For shades which cannot be produced with Azoic combinations in multicolour patterns, *e.g.* blues, greens, violets, greys, etc., the **Indigosols** are usually employed in preference to Vat colours, although the latter may be utilised if desired. The Indigosols, being oxidisable bodies, or, in other words, reducing agents, themselves act, to some extent, as resists under Aniline black pads. But their action in this respect, at the concentrations used in practice, is not sufficiently powerful, and requires to be supplemented by the addition of other resisting agents, which, whilst preventing the formation of Aniline black, do *not* prevent the development of the Indigosols. To bring about this result successfully implies a fine balance in the constituents of the resist colours, since it must not be forgotten that the formation of Aniline black and the regeneration of the original vat-dyestuff bases of the Indigosols are both prevented by reducing agents and alkalis, or the alkali salts of volatile organic acids. Hence, if these substances are employed in Indigosol resist colours, only sufficient must be used to act on the more easily resisted Aniline black, leaving the Indigosols to be preferentially oxidised, or developed, at the expense of the Aniline. The oxidising agent—sodium chlorate—is provided in the Aniline black padding liquor.

It is to be noted that ammonium sulphocyanide resists Aniline black efficiently and, at the same time, promotes the development of Indigosols in steaming. It is not, however, much used for this purpose in Aniline black resist styles.

The Naphthol A.S. resist process is worked as follows:—

(1) Pad the goods in Aniline black solution and dry gently in the hot flue so that they come out pale yellow in colour.

(2) Print the Naphtholate resists, dry.

(3) Steam the goods in the rapid ager for 3–5 minutes at 212° F. in a copious supply of dry steam.

(4) Develop the resist colours by passing the goods through a diazo solution in a padding machine or small roller vat; air well to give time for coupling, wash well, soap at the boil, wash, and dry.

The process works well and without difficulty if due care is paid to the conditions of steaming, and to the preparation of the resist colours and diazo solutions respectively.

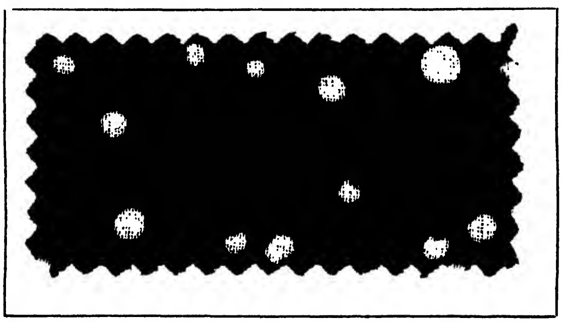
In making the Naphtholate resists, the Naphthols are dissolved in methylated spirit, caustic soda, and water. The use of methylated spirit greatly facilitates solution of the Naphthols, which generally dissolve completely in the cold; if not, they may be gently heated to 85°–105° F., but not beyond this point, as excessive heating with caustic soda causes decomposition with formation of sticky, resinous bodies which destroy the working qualities of the printing colours and render impossible the production of even shades.

The Naphtholate solution is then mixed with a zinc oxide-starch-tragacanth paste, and a further quantity of caustic soda is added carefully, in small portions, so as to avoid overheating. Zinc oxide prevents the printing colour from "flushing," *i.e.* spreading or running beyond the limits of the printed pattern, and also plays a small part in resisting the Aniline black pad ; the caustic soda acts as the principal resisting agent and, at the same time, holds the Naphthol in solution as naphtholate of soda, preventing its precipitation by the acid vapours which are evolved from the Aniline black during the steaming operation. An accumulation of acid vapours in the rapid ager is avoided by providing for a constant flow of steam through the chamber and by keeping the ventilators and exhaust trunk full open during the steaming process.

To facilitate the coupling of the diazotised bases with the printed naphthols, which is retarded by the strong alkali content of the latter, an addition of a sufficiency of acetic acid should be made to the developing solutions. Moreover, if the developing is done in a padding machine, it is very necessary to give the cloth a short, but not too short, air passage before squeezing, in order to allow sufficient time for the coupling reaction to complete itself. This can be done, without trouble, by interposing a series of rollers between the padding box and the squeezing bowls, whereby the saturated cloth is subjected for the necessary time to the action of the diazo solution. If this is not done the coupling will be incomplete and the resist colours will suffer in depth and purity.

On the other hand, special airing arrangements may be dispensed with if the steamed goods are given a passage of 40–60 seconds through the developing solution contained in an open box fitted with top and bottom guide rollers —*e.g.* the first compartment of an open soaping range—only sufficient solution being used to cover the bottom guide rollers. In this case the developing solutions may be reduced in strength and, in view of the greater volume of liquor in the dye bath, the added amount of acetic acid should be cut down.

Examples of these two methods of working are shown in the following patterns. The first pattern has been developed in a padding mangle; the second in a roller vat with a weak developing solution. In both instances the red is the same combination—Naphthol A.S.-D./Fast red K.B. base.



Naphthol A.S. Resists on Aniline Black Pad, Padding Machine Development (I.G.).

(1) Pad the cloth in—

Aniline Black Liquor.

$$\left\{\begin{array}{lll} 84 \text{ grms.} & \text{aniline salt.} & \\ 5 \quad ,, & \quad ,, & \text{oil.} \\ 200 \text{ c.c.} & \text{water.} & \end{array}\right.$$

54 grms. potassium ferrocyanide.
250 ,, water.
30 ,, sodium chlorate.
250 ,, water.
50 ,, tragacanth mucilage 65 : 1000.

To 1000 c.c.

Dry gently in hot air or over wrapped cylinders.

(2) Print the following resists :—

White Resist.

400	grms.	British gum thickening 1 : 1.
100	,,	caustic soda 77° Tw.
300	,,	potassium sulphite 90° Tw.
200	,,	water.
1000		

Red Resist.

40 grms. Naphthol A.S.-D.
60 ,, methylated spirit.
30 ,, caustic soda 90° Tw.
120 ,, warm water.

Dissolve (by gentle heat if necessary) and stir into a cold mixture of—

400 grms. thick starch-tragacanth paste.
150 ,, zinc oxide 50 per cent. paste.
5 ,, olive oil.
95 ,, water.
70 ,, caustic soda 90° Tw.

Mix thoroughly and add gradually—

30 grms. caustic soda 90° Tw.

1000

Yellow Resist.

As Red resist, but made with Naphthol A.S.-G., 35 grms. per kilo.

(3) Steam for 3 minutes in the rapid ager with dry steam at 212° F.

(4) Develop the Naphthol resists in a padding machine with an arrangement for airing the goods before squeezing.

Developing Solution K.B. 20.

20 grms. Fast red K.B. base.
150 c.c. cold water.
20 ,, hydrochloric acid 32° Tw.

Dissolve and stir vigorously into—

8 grms. sodium nitrite, dissolved in
40 c.c. cold water.

Allow to stand 20–30 minutes, filter, and add—

15 grms. sodium acetate.
60 c.c. water.
20 ,, acetic acid 50 per cent.

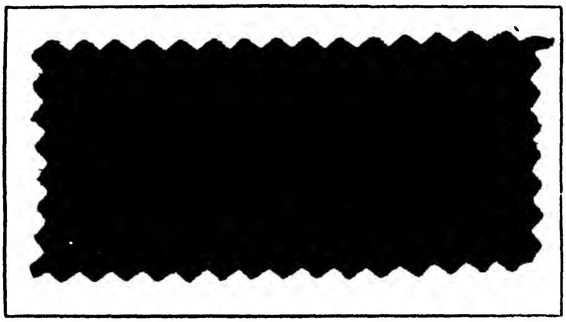
Make up to 1000 c.c.

After padding, the goods are aired for 40–60 seconds, then squeezed through the bowls of the padding machine and washed, soaped at the boil, washed, and dried.

The pattern below exemplifies the use of Indigosols for supplementing the Naphthol A.S. range in this particular style.

(1) The cloth is first padded in Aniline black solution and dried as before.

(2) Print with red and Indigosol green resists.



Naphthol A.S. and Indigosol Resists on Aniline Black Pad, Roller Vat Development (I.G.).

RED RESIST.

As for preceding pattern.

GREEN RESIST.

50	grms.	Indigosol green I.B.A. paste.
50	,,	Indigosol yellow H.C.G.
50	,,	Glyecine A.
5	,,	ammonia 25 per cent.
185	,,	water at 175° F.

Dissolve and stir into—

400	grms.	thick starch-tragacanth paste.
150	,,	water.
5	,,	ammonia 25 per cent.
40	,,	ammonium oxalate.
40	,,	potassium sulphite.
25	,,	sodium acetate.
1000		

A Blue resist may be made according to the same recipe merely by replacing the foregoing two dyestuffs with Indigosol O.6 B.; and other resists similarly.

(3) After printing, steam for at least 5 minutes to develop the Indigosols fully, along with the black ground.

(4) Develop the red resist in the roller vat with a reduced developer.

DEVELOPING SOLUTION K.B. 5.

1 part Developing Solution K.B. 20 (see preceding pattern).
3 parts water.

Allow a passage of about 50 seconds; wash, soap at the boil, wash, and dry.

In addition to the examples just described, the following multicolour combinations are obtainable on Aniline black padded cloth by the Naphthol A.S. resist process:—

For :—	Print :—	Develop with :—
Yellow. / Pink. / Red.	Naphthol A.S.-G. / ,, A.S.-O.L. / ,, A.S.-D.	Fast Scarlet R.C. base.
Yellow. / Orange. / Red.	Naphthol A.S.-G. / ,, A.S.-D. / ,, A.S.-T.R.	Fast Scarlet T.R. base.
Yellow. / Red.	Naphthol A.S.-G. / ,, A.S.-T.R.	Fast Red T.R. base.
Violet. / Brownish-Yellow.	Naphthol A.S. / ,, A.S.-G.	Fast Violet B. base.
Blue. / Brownish-Yellow.	Naphthol A.S. / ,, A.S.-G.	Fast Blue R.R. base.

If very light shades of the above colours are required it is advisable to use Indigosols in place of printed Naphtholates, which do not stand much reduction in strength.

Rapidogen (and Indigosol) Resists on Aniline Black Pads.—The Rapidogen dyestuffs, specially prepared and printed on cloth padded in Aniline black solutions, produce effects corresponding to those obtained by printing naphtholates ; and as each Rapidogen dyestuff contains in itself all the constituents necessary to the formation of the final colour, it follows that the employment of Rapidogens permits of the production of a much wider range of effects than is possible with the Naphthols. In spite of this, however, the Rapidogens are chiefly used for various shades of red, orange, yellow, and brown, other colours being obtained from Indigosols.

The cloth is padded with Aniline black and carefully dried in hot air, and then printed, as soon as possible, with the Resists made up according to the recipes in the following tables :—

Rapidogen Resists.

	1.	2.	3.	4.
	grms.	grms.	grms.	grms.
Rapidogen Red G.	80	..	..	..
,, Scarlet R.	..	80	..	..
,, Orange G.	..	..	80	..
,, Yellow G.	..	..	..	80
Caustic soda 72° Tw.	30	30	30	20
Methylated spirit	30	30	30	30
Lukewarm water	120	120	130	150
Neutral starch-tragacanth thickening	400	400	450	450
Zinc oxide 1 : 1	200	200	150	200
Sodium nitrite 20 per cent.	60	60	60	50
Glycecine A.	50	50	50	..
Potassium sulphocyanide	30	30	20	20
	1000 grms.			

INDIGOSOL RESISTS.

	1.	2.	3.	4.	5.	6.	7.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol O. 4 B.	20	..	..	..	..	..	..
,, Printing Violet I.B.B.F.	..	80	..	..	5	..	..
,, Green I.B.A. paste	..	..	80	..	..	..	..
,, Printing Blue I.G.G..	..	..	..	30	..	..	..
,, ,, Black I.B. (Grey)	..	..	..	..	20	..	..
,, Yellow H.C.G.	..	..	..	..	..	60	..
,, Printing Purple I.R.	..	..	..	..	..	..	70
Glyecine A.	..	60	60	..	50	50	60
Fixer C.D.H.	50	60	60	50	50	50	60
Indigosol Developer D.	50	..	..	50	..	..	..
Hot water	200	130	130	160	200	170	130
Neutral starch-tragacanth thickening	480	470	470	510	475	470	480
Add at 60° C.—							
Sodium acetate	140	140	140	140	140	140	140
Solvay soda	60	60	60	60	60	60	60
	1000 grms.						

After printing, the goods are steamed for 2–3 minutes in the rapid ager with dry steam at about 208°–212° F. to develop the black, the exhaust ventilator being kept full open. The resist colours are then developed by running the goods in the open width for 30 seconds through a bath of—

2–3 grms. bichromate of soda.
20 c.c. sulphuric acid 168° Tw.
30 ,, ammonium vanadate 1 : 1000.

To 1000 c.c.

at about 85°–90° F. The goods are then washed, soaped at the boil, washed, and dried.

Many other processes have been suggested, and used, for discharging (resisting) Aniline black, but most of them have become obsolete. The use of xanthates, sulphocyanides, etc., and of pigments fixed with glue or caseïn in combination with either hexamethylenetetramine or formaldehyde, has been practically discontinued, and processes founded thereon are now of no more than historical interest.

Resists under Aniline Black.

The resist method proper differs from the so-called discharge method of producing white and coloured effects on Aniline black, in that the resist colours are printed on *white* cloth *before* it is passed through the black bath. After printing, the goods are dried, padded in Aniline black, steamed, chromed, washed, soaped, and dried. The advantage of carrying out the operations in this order is, that the printed cloth may be kept in stock any reasonable length of time before padding in black,—an advantage which, besides simplifying the process, allows of a large number of pieces being dyed black at the same time. In working the discharge process, the production of the black padding machines must be arranged to balance, and must be kept down to, the consumption of the printing machines, for if more cloth is padded than

can be printed on the same day it is liable to become useless, especially in warm weather, owing to the partial development of the black. Hence the discharge process, though generally preferred for the best work, entails a good deal of organisation, demands the making of special arrangements, and requires constant supervision at every stage. On the other hand, the course of the reserve process runs more or less on the lines of the ordinary works routine; the reserve colours—containing nothing that is likely to deteriorate by several days' exposure to dry air—can be printed at any time, and the printed goods can then be kept until it is convenient to pad them in the black liquor.

For white resists, chalk or zinc oxide, together with soda-ash, sulphite of potash, acetate of soda, zinc, or magnesium, sulphocyanide of ammonia, and caustic soda, are the reagents most commonly employed.

The quantity of soluble matter is kept as low as possible to avoid all chance of the resists running during the subsequent padding; but chalk and zinc oxide do not give good results without the addition of other resisting substances, hence their inclusion.

Chalk is perhaps the best for white resists, but zinc oxide also gives satisfactory whites, and is always used for coloured resists on account of its conversion into the ferrocyanide, which acts as a mordant for Basic colours. A little albumen may be added to increase the fastness of the colours, but as a rule it is unnecessary, except, of course, in pigment resists.

Zinc Oxide-Basic Colour Resists.—The following recipes, taken from practice, will be ample to illustrate the principle of the resist process for Aniline blacks dyed on the padding mangle:—

Resist White R.S.

200	grms.	precipitated chalk.
50	,,	potassium sulphite 90° Tw.
50	,,	acetate of soda.
95	,,	water.
5	,,	Ultramarine blue. Beat into a smooth cream, and add—
600	,,	starch paste.
1000		

Grind the mixture before use.

Basic Colour Resists R.S.

	Red.	Pink.	Blue.	Yellow.	Green.	Violet.
Rhodamine 6 G. extra	16	8	..	..	..	..
Auramine O.	4	..	..	30	..	..
Rhodamine B.	..	8	..	..	..	28
Brilliant green	..	..	..	..	25	..
Thionine blue O.	..	..	20	..	..	..
New methylene blue N.	..	..	..	..	..	3·5
Glycerin	..	..	..	..	..	..
Water	100	100	100	100	150	100
Starch paste	230	234	230	220	175	218·5
Warm together, cool, and add—						
Paste R.S.	650	650	650	650	650	650
	1000	1000	1000	1000	1000	1000

A brighter green, which is more regular in working, is made up of New solid green 2 B. (Geigy) and Acridine yellow G.

GREEN R.S. 2.

20	grms.	Acridine yellow G.
9	,,	New solid green 2 B.
30	,,	glycerine.
170	,,	water. Dissolve, and strain into—
81	,,	warm water.
40	,,	starch. Boil, cool to 60°–70° C., and add—
650	,,	Paste R.S.
1000		

PASTE R.S.

170	grms.	zinc oxide.
100	,,	water.
20	,,	glycerine.
300	,,	starch paste 15 per cent.
30	,,	turpentine.
30	,,	bisulphite of soda 52° Tw.
650		

TYPE OF PIGMENT RESIST.

GREY R.S.

100	grms.	Ultramarine blue.
60	,,	lampblack.
150	,,	albumen solution 40 per cent.

Grind and add—

40	grms.	6 per cent. tragacanth.
650	,,	Paste R.S.
1000		

Print any of the above colours on white cloth, allow to lie a day or two in a warmish dry place, then pad (straight through the nip) in Black P., dry,

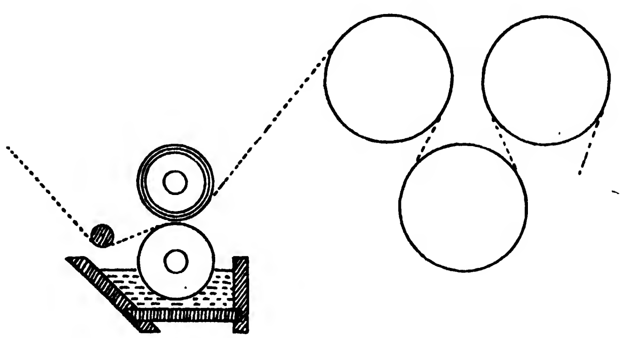
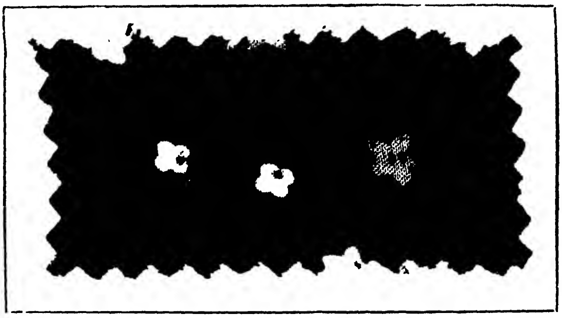


FIG. 85.—Padding machine for Aniline black resist styles.

steam 3–4 minutes in the rapid ager, chrome, wash, and soap in the open width.

The padding mangle has two bowls, the lower one of brass and the upper of indiarubber; the cloth runs with the printed side to the brass bowl, which revolves partly immersed in the padding liquor (Black P.), as shown in fig. 85.

Resist effects under printed covers of Aniline black can be obtained by analogous means. In the case of Pigment and Basic colours with zinc oxide, albumen is the fixing agent employed; while for Basic colours with acetate of soda, fairly good and bright results are produced with tannin, together with a little hydrosulphite and phenol.



(C.P.A.)

Zinc Oxide-Basic Colour Resists under Aniline Black.

(*a*) Pigment Resists under Printed Black Covers.

	Yellow I.	Yellow II.	Blue I.	Blue II.
Zinc oxide	80	..	80	..
Magnesium acetate 40 per cent.	150	..	150	..
Acetate of soda	..	150	..	150
Starch paste	120	100	..	..
6 per cent. tragacanth	200	200	220	300
Albumen 50 per cent.	150	150	150	150
Chrome yellow	300	400	..	..
Ultramarine blue	..	..	300	300
Water	..	..	100	100
	1000	1000	1000	1000

(*b*) Basic Colour Resists with Zinc Oxide and Albumen (under Printed Covers).

20 grms. Basic dyestuff.
100 ,, water.
30 ,, glycerine.
50 ,, 6 per cent. tragacanth.

Boil, cool, and add—

650 grms. Paste R.S.
150 ,, 50 per cent. albumen.

1000

(*c*) Basic Colour Resists under Printed Covers (Acetate of Soda, Tannin, etc.).

20 grms.	Basic dyestuff.	
30 ,,	glycerine.	
10 ,,	acetin.	
130 ,,	water.	

Dissolve and add to—

100 grms.	6 per cent. tragacanth.
240 ,,	water.
60 ,,	starch.

Boil and add—

50 grms. phenol.

Cool and add—

50 grms.	tannic acid.
75 ,,	Hydrosulphite N.F. conc.
80 ,,	water.
5 ,,	formaldehyde 40 per cent.
150 ,,	acetate of soda.
1000	

This recipe gives fast resists of sufficient brightness under either copper, vanadium, or prussiate black covers.

Print any of the above cover resists on white cloth ; dry, and over-print with Aniline black ; steam 2–4 minutes, chrome, wash, soap, wash, and dry. The Basic colour resists fixed with tannin are passed through tartar emetic before chroming.

Azoic Colour Resists under Aniline Black.—The earliest method of obtaining Azoic colour resists under padded or printed Aniline black was worked out by Pluzanski, who utilised the resisting properties of insoluble carbonates precipitated on the fibre. The carbonates themselves cannot be printed as such, since they would be washed out in process. Pluzanski's method yields excellent results and, until the introduction of the Rapid Fast and Rapidogen dyestuffs, was the only one available for the purpose, but it is complicated and slow in operation and has now given place to newer and more convenient methods. As an example of the ingenious means adopted by older calico printers to overcome technical difficulties now no longer existing, and for its historical interest as the harbinger of a current style of great importance, the Pluzanski process is worthy of description. It is carried out in the following manner.

A diazo solution containing acetate of lime, zinc, or lead is printed on naphthol-prepared cloth. The cloth is then passed through a solution of soda-ash or gaseous ammonia (which precipitates the carbonate or oxide respectively of the metal), and finally well washed to remove all traces of β-naphthol and alkali. After drying, the goods are printed or slop-padded with Aniline black, steamed, washed, etc., and dried.

White, red, and claret resists are obtained by the use of acetate of lime (or zinc, if they are unassociated with lead yellows), and yellow by means of lead acetate. Basic colours may also be employed for pink, green, and blue if printed with zinc oxide and albumen.

Prussian blue and a green obtained from a mixture of Prussian blue and Chrome yellow are also producible by printing ferrous acetate and a mixture

of ferrous and lead acetates, followed by suitable treatments to develop the colours.

For white and Azoic colour resists alone the process consists of the following sequence of operations :—

(1) Pad the cloth in a 3 per cent. β-naphthol prepare. Dry.
(2) Print on white, red, claret, or orange resists. Dry.
(3) Pass the goods through a tepid solution of soda-ash.
(4) Wash in warm water to remove the naphthol and alkali.
(5) Dry, and cover or slop-pad in Aniline black solution.
(6) Dry, and steam 2–3 minutes in the rapid ager.
(7) Wash, soap, and dry.

The treatment in soda-ash converts the acetates of zinc, lime, and lead contained in the resists into insoluble carbonates which withstand the subsequent washing operations, and thus act as reserves under the black. If necessary, they may be removed completely after steaming by a short treatment in dilute acid.

For Chrome yellow and Prussian blue resists in combination with the above, the cloth, after steaming, is chromed in—

1000	parts	water.
150	,,	sulphate of soda.
10	,,	bichromate of soda.

Neutralise with ammonia and use at 50° C.

Then wash, pass through a slightly acidulated solution of potassium ferrocyanide to develop the Prussian blue, wash again, and re-chrome (if necessary) in a slightly acid ½ per cent. solution of bichromate, wash and dry.

For the production of a white, red, claret, blue, yellow, and green effect on a black ground the following colours may be employed :—

Resist Yellow :—

250	grms.	lead acetate.
600	,,	water.
150	,,	British gum.
1000		

Boil and cool.

Resist Blue :—

450	grms.	ferrous acetate 30° Tw.
400	,,	acetate of lime 30° Tw.
100	,,	British gum.
50	,,	starch.
1000		

Boil and cool.

Resist Green :—

200	grms.	acetate of lead.
150	,,	ferrous acetate 30° Tw.
75	,,	acetate of zinc.
400	,,	water.
175	,,	British gum.
1000		

AZOIC COLOUR RESISTS.

	ORANGE.	RED.	CLARET
Metanitraniline	28 grms.	..	..
Paranitraniline	..	22 grms.	..
α-Naphthylamine hydrochloride 36 per cent.	..	..	70 grms.
Hydrochloric acid 36° Tw.	44 c.c.	35·2 c.c.	29 c.c.
Hot water	150 ,,	100 ,,	..
Dissolve, cool, and add—			
Ice water	90 ,,	124·8 ,,	143·5 ,,
Ice	36 grms.	75 grms.	120 grms.
Nitrite solution (28 per cent. $NaNO_2$)	52 c.c.	43 c.c.	37·5 c.c.
Filter into—			
Resist paste L.P.	600 grms.	600 grms.	600 grms.
Make up to	1 litre.	1 litre.	1 litre.

RESIST PASTE L.P.

4000 grms. acetate of lime 30° Tw.
1000 ,, 10 per cent. gum tragacanth thickening.
900 ,, starch. Boil, cool, and make up to 6 litres with acetate of lime 30° Tw.

Print the above six colours on naphthol-prepared cloth ; pass through a warm bath of soda-ash ; well wash in warm water ; dry; print a cover pattern in Aniline black ; steam 2–3 minutes in the rapid ager ; pass through gaseous ammonia to neutralise the acidity of the cloth, and to re-precipitate any oxide of iron that may have been converted into chloride ; chrome in a neutral bath of bichromate and sodium sulphate to fix the lead salts ; soap lightly, wash well, and develop the blue by a run through an acidulated 2 per cent. solution of yellow prussiate of potash ; wash well again, and chrome a second time in—

5 grms. bichromate of soda
7½ ,, sulphuric acid 168° Tw. } at 50° C.
1000 ,, water

Finally, wash well in warm water, then in cold running water, and dry.

Basic colour resists for working along with the foregoing colours require no special description, since they consist merely of zinc oxide, dyestuff, albumen, and thickening. After printing, they are steamed 2–3 minutes to coagulate the albumen, and the goods are then treated exactly as above. Basic colours are used only in conjunction with Azoic colours, and sometimes with Chrome yellows, not with Prussian blue.

RAPIDOGEN AND RAPID FAST COLOUR RESISTS UNDER ANILINE BLACK.—Neither the Pluzanski process nor the Naphtholate printing process of obtaining Azoic colour resists under Aniline black was entirely satisfactory from a practical printer's point of view. The first was slow and required careful supervision ; the second entailed the use of relatively strongly alkaline printing colours with its attendant drawbacks ; and both, although yielding bright effects, were strictly limited, in practice, to the production of combinations in yellows, oranges, and reds. With the introduction of the Rapid Fast and Rapidogen dyestuffs these limitations and disadvantages have been, more or less, overcome ; the process has been simplified and the range of effects greatly extended without the use of other classes of dyestuffs. The latter are not excluded, however, and may be used for special shades of blue, green, or

violet and for all *pale shades* of these colours and oranges and pinks. Very light shades are not often required in Aniline black resist styles ; when they do form part of a colouring they are better obtained with Indigosols or Vat colours ; Azoic dyestuffs are best adapted for full, rich, and brilliant colours, whereas the Indigosols are excellently suited for pale shades, apart from which they are unnecessary and, also, too expensive for dark shades in these styles. The outstanding advantage of using Rapid Fast and Rapidogen dyestuffs for resists under Aniline black is that they require no previous preparation of the cloth in naphthols nor any subsequent development with diazo solutions. They are stable mixtures of naphthol and base, which are simply printed on white cloth, padded with Aniline black, and finished off by steaming, chroming, and soaping in the usual manner.

The *Rapid Fast Colours* give excellent results so far as they go, but the range is lacking in blues, greens, and violets suitable for resist effects and, in some cases, too, they are not sufficiently fast to rubbing. They are cheaper than Rapidogens and, for this reason, they find considerable employment for the production of fast and bright reds, oranges, and yellows in styles where no great variety is demanded.

The *Rapidogen Colours*, on the other hand, comprise a full range of shades and, when applied by a process recently perfected by the I. G. Farbenindustrie A.G., they yield very bright and rich resist effects of good all-round fastness, and especially to rubbing, and they permit of the production of a great variety of all-Azoic multicolour combinations, including violet, blue, green, and brown shades hitherto unobtainable as resists in these colours on Aniline black grounds.

In preparing the printing colours, according to the recipes given in the following tables, the dyestuff is pasted up or dissolved with a mixture of water, methylated spirit, and caustic soda and stirred into the thickening. The other ingredients are then added and well incorporated, and the finished colour is allowed to stand overnight if possible. This is not absolutely essential, but it is of advantage in respect of easy working and good yield of colour.

RAPIDOGEN COLOUR RESISTS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Rapidogen Yellow G.	80	..	..	..	..	..	..	..	..	..
,, Orange G.	..	80	..	..	..	..	..	..	..	..
,, Scarlet R.	..	..	80	..	..	..	..	..	..	..
,, Red G.	..	..	..	80	..	..	..	..	..	..
,, ,, R.	..	..	..	..	80	..	..	..	..	..
,, ,, I.R.	..	..	..	..	..	25	80	..	..	..
,, Bordeaux R.	..	..	..	..	..	..	..	50	..	..
,, Corinth I.B.	..	..	..	..	..	..	..	..	50	..
,, Violet B.	..	..	..	..	..	..	..	..	..	30
Caustic soda 70° Tw.	30	30	30	30	30	30	30	30	30	30
Methylated spirit	30	30	30	30	30	30	30	30	30	30
Water (lukewarm)	100	100	100	100	100	100	100	100	100	100
Neutral starch-tragacanth thickening	500	500	500	500	500	500	500	550	500	550
Zinc oxide 1 : 1	120	120	120	120	120	120	120	120	120	..
Calcined magnesia 1 : 1	..	..	..	..	..	..	..	..	..	120
Neutral chromate solution	..	..	..	..	..	..	..	50	..	..
Water (cold)	140	140	140	140	140	195	140	70	170	140
	1000 grms.									

	11.	12.	13.	14.	15.	16.	17.	18.	19.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Rapidogen Blue R.	30	..	..	..	..	..	..	..	..
,, ,, B.	..	25	..	..	..	..	..	..	..
,, Brown I.R.	..	..	60	..	..	..	..	..	..
,, ,, I.B.	..	..	..	60	..	..	..	..	..
,, Olive Brown I.G.	..	..	..	..	40	60	..	..	..
,, Green B.	..	..	..	..	..	..	60	30	60
Naphthol A.S.-G.	..	..	..	..	..	..	..	3	5
Caustic soda 70° Tw.	30	30	30	30	30	30	30	30	30
Methylated spirit	30	30	30	30	30	30	30	30	30
Water (lukewarm)	100	100	100	100	100	100	100	100	100
Fibrit D.	30	50	..	..	..	..	50	50	50
Neutral starch-tragacanth thickening	550	550	500	500	500	500	450	450	450
Zinc oxide 1 : 1	..	..	120	120	120	120	120	120	120
Calcined magnesia 1 : 1	120	120	..	..	..	..	..	..	..
Urea	50	50	..	..	..	..	30	30	30
Water (cold)	60	45	160	160	180	160	130	157	125
	1000 grms.								

NEUTRAL CHROMATE SOLUTION.

150 grms. bichromate of soda cryst.
716 ,, water.
134 ,, caustic soda $32\frac{1}{2}$ per cent. (=70° Tw.).

1000

WHITE RESISTS.

	I.	II.
Starch-tragacanth paste	545 grms.	500 grms.
Zinc oxide 1 : 1	350 ,,	250 ,,
Ultramarine	5 ,,	5 ,,
Potassium sulphite 90° Tw.	50 ,,	..
Sodium acetate	50 ,,	..
Sodium thiosulphate	..	80 ,,
Caustic soda 70° Tw.	..	80 ,,
Water	..	85 ,,
	1000	1000

Two examples will serve to illustrate the preparation of Resists from Rapid Fast colours.

RAPID FAST COLOUR RESISTS.

	Yellow.	Red.
Rapid Fast yellow G.G.H. powder	100 grms.	..
Rapid Fast scarlet L.H. powder	..	80 grms.
Caustic soda 72° Tw.	30 ,,	30 ,,
Methylated spirit	30 ,,	30 ,,
Lukewarm water	150 ,,	150 ,,
Neutral starch-tragacanth paste	400 ,,	400 ,,
Zinc oxide	75 ,,	75 ,,
Water	215 ,,	235 ,,
	1000	1000

After the white cloth has been printed with the foregoing Resists, it is well dried, and then padded with the *printed side downwards* through the following Aniline black solution:—

Aniline Black Padding Liquor.

(A.)	2500	c.c.	water.
	900	grms.	aniline salt.
	50	,,	aniline oil.
	500	,,	tragacanth mucilage 60 : 1000.
(B.)	550	,,	potassium ferrocyanide.
	2500	,,	water.
(C.)	300	,,	sodium chlorate.
	1200	,,	water.
(D.)	400	,,	acetic acid 50 per cent. (12° Tw.).
	100	,,	formic acid 85 per cent.

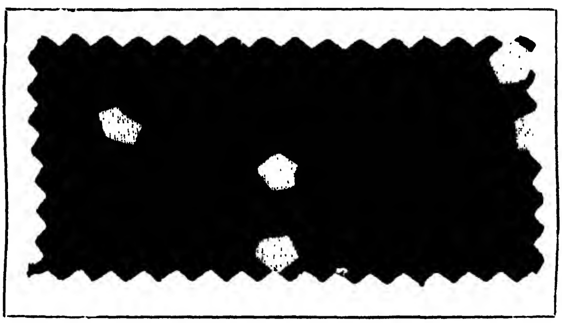
Mix (A.), (B.), (C.), and (D.) just before use and make up to—

10 litres

The goods are padded, straight through the nip, between the bowls of a two-bowl padding mangle, the lower bowl being wrapped with calico or lapping and revolving partly immersed in the Aniline black liquor (see fig. 85), and are then immediately dried on a cylinder drying machine. If the goods are padded on the back, *i.e.* with the printed side in contact with the upper bowl, the resists will neither be so bright nor so full as when padded on the face. The temperature of the drying cylinders must be adjusted to ensure a thorough drying of the padded cloth, which ought to display an olive green appearance as it leaves the machine. During this drying operation the Rapidogen and Rapid Fast colours are completely developed under the combined influence of heat and the organic acids added to the Aniline black padding liquor. The process is completed by steaming the goods for 2–3 minutes in the rapid ager with dry steam at about 208° F., after which they are chromed in the open soaper at 120° F. with—

2	grms.	bichromate of potash.
4	,,	soda-ash.
1000	,,	water,

washed, soaped at the boil, washed, and dried.



(I.G.)

Rapidogen Red G. (No. 4, p. 795) } Resisted under
White Resist II. (p. 796) } Aniline Black.

The Indigosol dyestuffs, as already noted, may be associated with Rapidogen colours in multicolour combinations for the production of bright blues and greens, and for light shades that are not obtainable satisfactorily from Rapidogen colour resists under Aniline black.

Indigosol Resists under Aniline Black.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol Golden Yellow I.G.K.	10	..	..	..	..	..	..	..	..	..	..
Indigosol Pink I.R. extra	..	15	..	..	..	..	..	..	..	..	..
,, Brilliant Pink I. 3 B.	..	..	15	..	..	..	..	..	..	..	..
,, Brown I.R.R.D.	..	..	..	10	..	..	..	..	..	..	..
,, Printing Violet I.B.B.F.	..	..	..	..	15	..	..	..	..	..	..
Indigosol O. 4 B.	..	..	..	..	..	15	..	..	..	..	..
,, O. 6 B.	..	..	..	..	..	..	10	..	..	..	..
,, Printing Blue I.B.	..	..	..	..	..	..	..	20	..	..	..
,, ,, ,, I.G.G.	..	..	..	..	..	..	..	..	20	..	..
,, Green I.B.A. paste	..	..	..	..	..	..	..	..	..	20	..
,, Printing Black I.B.	..	..	..	..	..	..	..	..	..	..	15
Glyecine A.	30	30	30	30	30	30	30	30	30	30	30
Hot water	380	375	375	380	375	375	380	370	370	370	375
Neutral starch-tragacanth thickening	400	400	400	400	400	400	400	400	400	400	400
Zinc oxide 1 : 1	150	150	150	150	150	150	150	150	150	150	150
Caustic soda 72° Tw.	30	30	30	30	30	30	30	30	30	30	30
	1000 grms.										

Green Mixture from Indigosol Green I.B.A. and Rapid Fast Yellow G.G.H.

Indigosol Green I.B.A. paste	20 grms.	(A.)
Glyecine A.	30 ,,	
Water	150 ,,	
Neutral starch-tragacanth thickening	200 ,,	
Rapid Fast Yellow G.G.H.	80 ,,	(B.)
Caustic soda 72° Tw.	30 ,,	
Methylated spirit	30 ,,	
Lukewarm water	100 ,,	
Neutral starch-tragacanth thickening	200 ,,	
Zinc oxide 1:1	150 ,,	
Cold water	10 ,,	
	1000	

Print the resists on white cloth alone or along with Rapidogens, pad in Aniline black, dry over cylinders, and steam as described for Rapidogens and Rapid Fast colours ; then chrome as under, instead of by the method given above. Pass the goods for 30 seconds at 20°–30° C. through a bath of—

2–3 grms. bichromate of soda.
20 c.c. sulphuric acid 168° Tw.
30 ,, vanadate of ammonia 1 : 1000.
1000 ,, water.

The Indigosols are developed fully during this treatment. Wash, pass through a 0·2 per cent. solution of soda-ash, wash, soap at the boil, wash, and dry.

A slightly better yield of the Indigosols is said to be obtained, especially in the darker shades, by using zinc acetate as resisting agent in place of zinc oxide and caustic soda. About 200 grammes of zinc acetate (dry) per kilo. of printing colour is a suitable proportion for general work.

Combinations of Rapidogen and Indigosol dyestuffs afford the only means available for the production of Resist effects under Aniline black which are, at the same time, fast and bright.

So far, the Soledon dyestuffs do not appear to have been applied in practice to resist styles, but there is no reason why they should not be so applied. They are all derived from anthraquinonoid dyestuffs, and are faster even than the Indigosols which, with one exception, are derivatives of Indigoid dyestuffs. They are as yet, however, of very limited range and not particularly bright as a class, although Soledon yellow G. and Soledon jade green are both satisfactory in this respect.

Vat and Sulphur Colour Resists under Aniline Black Pads.—For the production of coloured resists of great fastness under Aniline black, the Vat dyestuffs and, to a less degree, the Sulphur colours, are particularly suitable on account of their mode of application in alkaline media.

The ordinary printing colours, used for white ground prints, may be employed for resist work in many cases, especially if they contain China clay, which acts as a preventive to spreading or running. The best results, however, are obtained from colours containing a fairly large proportion of zinc oxide or levigated chalk, preferably the former, which works better in printing.

The procedure follows the same course, essentially, as that of other Aniline black resist styles. The white goods are printed, steamed, padded through Aniline black liquor, steamed again, and finished as usual.

The following process, taken from practice, is typical of the methods in general use and, of course, may be modified as required. As it stands it is suitable for patterns embodying fine details, such as stems of flowers, etc.; for heavy objects the zinc oxide content may be reduced.

Vat Colour Resists.

Scarlet.

3	kilos.	Ciba Scarlet G. paste.
6	litres	Resist paste V. (below).
1·5	kilos.	potassium carbonate.
0·5	litre	British gum thickening.

Heat to 120° F. to dissolve the carbonate, add—

0·3 litre caustic soda 90° Tw.

and make up to—

10 litres

Yellow as Scarlet, but with Indanthrene Yellow G.O.K. paste;
Crimson ,, ,, ,, Durindone Red B. or 3 B. paste;
Violet ,, ,, ,, Ciba Violet B. paste;
Green ,, ,, ,, Caledon Jade Green G.S. paste;

and various mixtures of these.

Resist Paste V.

$\begin{cases} \text{2 kilos. Formosul or Rongalite C.} \\ \text{1·2 litres light British gum thickening 1 : 2.} \end{cases}$
$\begin{cases} \text{2 kilos. zinc oxide.} \\ \text{2·4 litres light British gum thickening 1 : 2.} \end{cases}$

Dissolve the Formosul, mix the zinc oxide into a fine paste, add the two together and make-up to—

6 litres

Grind before use.

Any suitable Indanthrene, Caledon, Ciba, or Cibanone dyestuff may be utilised in the same manner, due note being taken of its concentration, *i.e.* whether it be a single or double paste, or in powder form.

The white goods, printed with the foregoing resists, are steamed for 4 minutes in the rapid ager at 212°–214° F. with not too damp steam, padded in Aniline black liquor, *with the printed side upwards*, between the bowls of a two-bowl padding mangle, dried immediately on cylinders, and then steamed again for 2–3 minutes in the rapid ager, and thereafter chromed, soaped at the boil, washed, and dried.

As resists on plain black grounds, the Vat and Sulphur colours are somewhat difficult to obtain free from halos. These halos, which sometimes impart a very attractive appearance to the prints, appear as white edges around the printed objects, and are due to the running, or bleeding out, of the soluble alkalies during the steaming process. Something may be done to prevent their formation by adding an excess of acid to the Aniline black liquor—say 10 grms. tartaric acid or 20 grms. lactic acid per litre—but they are difficult to prevent entirely, and for this reason the Vat colours have never been very largely employed for this class of work. The same may be said of the Sulphur colours, which are still less used on black grounds. Both classes have been almost entirely replaced by Rapidogens and Indigosols. Nevertheless, the Vat colours are capable of yielding excellent results in experienced hands and in works where the steaming conditions are favourable, and much good work is executed by their means.

Aniline Black "Cover" Styles.—For the most part the Vat and Sulphur colours are employed as resists under printed covers of Aniline black; they may also be used to "discharge" previously padded cloth, but practical difficulties have restricted their use in this direction. In combination with Rapidogen resists, the Vat and Sulphur dyestuffs produce a variety of effects of great fastness under black covers. The Indanthrene and Caledon colours, in particular, are of extreme fastness and of considerable brightness, whereas the Sulphur colours are mostly rather dull and, whilst fast to soaping, acids and alkalies, are generally only moderately fast to light and easily destroyed by the action of chlorine.

In applying the Vat dyestuffs, any of the ordinary alkali-sulphoxylate printing colours used for white ground styles may be used under printed covers. If the cover or over-print of Aniline black is heavy, the resisting effect of the under-print may be increased by the addition of sodium acetate, potassium sulphite, extra alkali or sulphoxylate, as required; as a rule potassium sulphite is used for this purpose. Recipes for suitable colours prepared from all types of Vat dyestuffs have already been given and need not be repeated here.

The following example of a Sulphur colour resist for cover styles illustrates the general procedure of preparation:—

SULPHUR COLOUR RESIST.

$\begin{cases} \text{25 grms. Thional brilliant green 3 G. conc. (Sandoz).} \\ \text{150 ,, water.} \\ \text{50 ,, caustic soda 77° Tw.} \\ \text{25 ,, sodium hydrosulphite conc. } (Na_2S_2O_4). \end{cases}$

Mix and add—

$\begin{cases} \text{200 grms. British gum paste 1 : 2.} \\ \text{100 ,, China clay 50 per cent. paste.} \end{cases}$

Heat the whole to 120°–140° F. and stir into—

$\begin{cases} \text{350 grms. caustic soda 77° Tw.} \\ \text{100 ,, light British gum (dry).} \end{cases}$

Heat again to 120° F. until the paste is smooth, cool before use, and make up to—

1000 grms.

The white cloth, printed with Vat or Sulphur colour resists, is dried and cover-printed with Aniline or Diphenyl black, then steamed *twice* for 2–3 minutes in the rapid ager and finally chromed, soaped, washed, and dried as usual. A rather better yield of colour, and generally sounder work, are obtained by steaming the resists *before* covering, followed by a second steaming, after covering, to develop the black.

Although the cover style just described is not in general use, it is nevertheless employed by several eminent firms in the production of specialities, in fast colours, on shirtings and dress goods, and it is a valuable process for such purposes.

Resists under Paramine Brown.

During the course of a series of experiments on the oxidation of various amines and diamines, Grandmougin discovered that paraphenylenediamine yielded an excellent brown of great fastness. The use of *p*-phenylenediamine as a brown colouring matter was patented in 1905, and the base is put on the market under the name of "Paramine brown."

Paramine brown is produced from paraphenylenediamine in a manner analogous to that by which Aniline black is obtained, and like that colour it must be produced upon the fibre by a process of oxidation. It yields a fine pure shade of brown, fast to air, light, and soap, and fairly fast to chlorine.

Being an oxidation product, Paramine brown can be resisted by means of reducing agents. Alkalies, acetate of soda, and zinc oxide also prevent, to a certain extent, the development of the colour, but they give imperfect whites, and can therefore only be used in combination with reducing agents. Of these latter, the most efficient are the stable sulphoxylate-formaldehyde compounds and sulphite of potash. A mixture of sulphoxylate and sulphite gives a purer white than sulphoxylate alone.

Coloured resists are obtained with Basic colours in conjunction with tannin, aniline oil, resorcin or phenol, and Rongalite (sulphoxylate-formaldehyde). Colours like Modern violet, Blue 1900, Phenocyanine, etc., which form leuco compounds on reduction, and also Persian berries extract, may also be employed for the production of fast-coloured resists. As a rule, however, the brighter Basic colours are preferred.

The resists are printed on cloth padded in a solution of Paramine brown, containing the necessary oxidising agents. After drying, the printed goods are steamed in the rapid ager, passed through a tartar emetic bath for the

fixation of Basic colours, well washed, soaped, and dried. The whole series of operations is carried out in the open width and in a continuous manner (after steaming).

As in the case of Aniline black styles, the resists under Paramine brown must be printed on freshly padded cloth, otherwise imperfect resists will be obtained. The other precautions mentioned in connection with Aniline black styles also apply equally to Paramine browns.

Resist effects in white and colours under printed covers of Paramine brown are obtained by printing the reserve pastes on white cloth, drying well, and then printing an all-over cover pattern in a thickened brown mixture of similar composition to the padding liquor. The goods are afterwards steamed and treated as above.

Resist effects on a plain ground of Paramine brown are produced by the following series of operations:—

1. Pad the bleached cloth in Brown P.

Brown P.

20	grms.	Paramine brown.
300	,,	hot water.

Dissolve and add—

400	grms.	cold water.
1·5	,,	Rongalite C.

Cool and add—

20	grms.	chlorate of soda.
50	,,	water.
20	,,	ammonium chloride.
2·5	,,	tartar emetic.
100	,,	water.
37·5	,,	glycerine.
15·5	,,	vanadium solution 1/1000 (see Mordants).

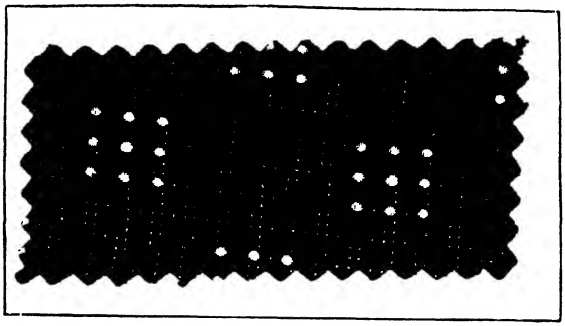
Make up to 1 litre with water.

Allow to stand one hour or until colourless; then filter through calico and pad the cloth; dry at 45°–50° C. in hot air. The addition of Rongalite reduces the oxidation products always present to a slight extent in commercial Paramine brown; and the tartar emetic has the useful property of retarding the oxidation of the padded cloth for 18 to 24 hours. Made as above, the padding liquor itself will keep in good condition for 48 hours.

2. On the padded and dried cloth print any of the resist pastes given below. Dry.

Resist Whites.	I.	II.
British gum paste	750 grms.	..
Rongalite C.	250 ,,	150 grms.
Acetate of soda	..	100 ,,
Sulphite of potash 90° Tw.	..	250 ,,
British gum	..	200 ,,
Water	..	300 ,,
	1000	1000

No. II. gives the better white.



Resist under Paramine Brown pad. (I.G.).

COLOURED RESISTS WITH BASIC DYESTUFFS.

	PINK.	YELLOW.	BLUE.	GREEN.
Rhodamine 6 G. extra	10	..	..	..
Thioflavine T.	..	20	..	15
Thionine blue G.O.	..	..	25	5
Glycerin	40	40	35	40
Acetin	20	40	40	40
Water	100	100	100	100
Starch-tragacanth paste	230	200	200	200
Dissolve, cool, and add—				
50 per cent. solution of tannin in alcohol	100	100	100	100
Resist Paste R.G.	500	500	500	500
	1000	1000	1000	1000

RESIST PASTE R.G.

$\left\{\begin{array}{l}\text{20 grms. starch.}\\ \text{90 ,, water.}\end{array}\right.$

340 ,, 6 per cent. tragacanth thickening.

150 ,, aniline oil.

Boil, cool to 60° C., and add—

400 grms. Rongalite C.

1000 Stir until the paste is perfectly smooth, and then cool.

Some Rhodamine pinks require a long exposure to the air before they develop to their full shade. Where this is inconvenient, the Discharge Pink (Erythrosin) used for Azoic colour discharging may be employed.

3. After printing the resist pastes, the cloth is steamed 4 to 5 minutes in the rapid ager.
4. Pass through a 1 per cent. to 2 per cent. solution of tartar emetic.
5. Wash in running water.
6. Soap at 60°–70° C.
7. Wash.
8. Dry over cylinders.

Operations 4, 5, 6, 7, and 8 are conducted in the open soaping range, and in a continuous manner.

For resists on figured grounds (printed covers) of Paramine brown, the same reserve pastes are applicable. Print white and colours on bleached cloth ; dry well ; cover in a printing paste of Paramine brown ; dry, steam, fix in tartar emetic, and wash, soap, wash and dry as above.

BROWN P. (FOR PRINTING).

100	grms.	starch.
30	,,	British gum.
503	,,	water.

Boil, turn off steam, and add—

25	grms.	Paramine brown.
2	,,	Rongalite C.
175	,,	boiling water.

Cool and add—

25	grms.	chlorate of soda.
40	,,	water.
30	,,	nitrate of ammonia.
50	,,	water.
20	,,	vanadium solution 1/1000.
1000		

Brown P. printing paste will withstand a prolonged steaming, and may therefore be used as a blotch in the ordinary steam styles.

An alternative and very convenient method for producing resists under a plain ground of Paramine brown is to print first resists consisting of zinc oxide and sulphite of potash, and then, after drying, to pad the goods through Brown P. (page 802). Coloured effects are obtained with any colouring matters that withstand sulphite of potash. The process is practically identical with the Aniline black resist processes.

Fuscamine (*m*-aminophenol) and Ortamine (*o*-anisidine) both yield useful dark browns when applied by the Paramine brown processes.

Resists under Slop-padded Sulphur and Vat Colours.

Owing to the several drawbacks attendant upon the use of oxidation discharges for the production of white and coloured effects on dyeings of the Sulphur colours, many attempts have been made from time to time to devise a practical method of obtaining similar and more satisfactory results by the reverse process, namely, by reserving or resisting the dyestuffs during the operation of dyeing.

Certain metallic salts possess the property of preventing the fixation of Sulphur colours on the fibre, and on this fact is based the resist process patented by the firm of Leopold Cassella & Co. (Eng. Pat. 12540, 1901).

This process depends upon the employment of zinc salts, which not only give exceedingly good resists, but also have no injurious action on the strength of the cloth. Other salts, such as those of manganese, cadmium, iron, tin, and aluminium, are similarly effective for certain styles of work, but none of them is quite so effective as the zinc salts, nor is any of them applicable to so many varieties of coloured reserves.

The two zinc salts which naturally suggest themselves as most suitable for the purpose are just those which yield the best results—namely, the sulphate

and the chloride. The use of sulphate of zinc formed the subject-matter of Cassella's first patent, but later on it was found that the chloride gave much superior results, and consequently it has replaced the sulphate almost entirely.

The resisting action of zinc and other metallic salts is due to their property of precipitating the Sulphur colours from their solutions in alkali and sodium sulphide. What really takes place has not been definitely ascertained, but it is probable that they combine with the dyestuff to form insoluble metallic leuco compounds of the colour.

This supposition, however, does not afford a complete explanation of their action, since it has been proved that different salts of the same metal, when used in quantities corresponding to equal weights of the same oxide, yield widely different results in practice.

Salts possessing strongly marked acid properties invariably give the best resists; hence the acid character of a salt doubtless determines, to a great extent, its suitability as a resisting agent. At the same time the base is also an important factor, for similar salts of different bases by no means behave alike towards the Sulphur colours.

The salt in which the combined resisting action of base and acid is most pronounced is zinc chloride—a product which, owing to its great solubility, is particularly well adapted to the production of resist effects with comparatively fine patterns, under dark shades of Sulphur colours. It is noteworthy that zinc chloride, although it possesses strongly acid properties, has no detrimental action on the fibre, unless, of course, it contain free mineral acid. The absence of free acid ought to be ensured before the resist pastes are prepared.

The dyeing of resist styles is best carried out in a continuous manner by giving the printed goods a single run through a padding machine, provided with a comparatively small colour box. In this way dark shades of blue, brown, green, and even black may be obtained of excellent fastness; and the short immersion of the fabric in the dye liquor has the advantage, over other methods, of allowing no time for the reserving agents to dissolve in the dye bath, and thus throw the colouring matter out of solution.

In order to obtain the best results with regard both to the sharpness of impression and purity of the resist effects, and to the thorough and uniform absorption of the dye liquor by the material, it is recommended by Baumann and Thesmar (*Zeitschrift für Farben-Industrie*, April 15, 1908) to dissolve the Sulphur dyestuff in glucose and caustic soda, rather than in sodium sulphide or hydrosulphite and caustic soda.

Padding liquors containing sodium sulphide are at once the least satisfactory and the most difficult to use: on the one hand, any excess of sodium sulphide, however slight, has the effect of dulling the white and coloured resists, whereas, on the other hand, a deficiency of sodium sulphide causes uneven dyeing by reason of the fact that the zinc chloride resists dissolve in the dye liquor, and by combining with the solvent to form zinc sulphide, precipitate the colouring matter in the dye bath. Even under the most favourable conditions, sodium sulphide dye baths yield inferior results to those obtained from either the hydrosulphite or glucose solutions. Hence the use of sodium sulphide is not to be recommended, except in cases where the alternative methods are inadequate.

On the contrary, the hydrosulphite-alkali and the glucose-alkali processes of dyeing Sulphide colours are easy of application, and require no more than ordinary care. With both, excellent resist whites (by the zinc chloride method) under full and level shades are readily obtained; and with neither is any pre-

cipitation of colouring matter in the dye bath to be feared, since a considerable excess of either alkali or reducing agent has, practically speaking, no detrimental effect on the resist pastes. So far as the production of good whites and uniform ground colours are concerned, there is little to choose between the two processes; but the glucose-caustic soda dye bath has the advantage of being more stable than the hydrosulphite-caustic soda bath, and is therefore preferable on economical grounds. If anything, too, the glucose process gives slightly better results than the other.

An important operation in the dyeing of Sulphur colours is the steaming of the goods in the *wet* state after padding. The actual dyeing of the material is not effected during the padding, but by the subsequent oxidation on the fibre of the reduced dyestuff it has absorbed. Formerly the padded goods were given a more or less prolonged exposure to the air to bring about the necessary re-oxidation, but this has now been replaced by a short steaming in a mixture of low-pressure steam and warm air. Under the influence of steam, the dye liquor penetrates the fibre more evenly and thoroughly, the colour is more completely developed, and darker, richer, and faster ground shades are obtained without in any way affecting either the purity of the resists or the strength of the fabric. With equal quantities of dyestuff, the shade produced by steaming is often twice the depth of that produced by air oxidation, so that, apart from its other technical advantages, it is by far the most economical process to employ, since it allows of the dyestuff being utilised to the utmost advantage.

The method of applying the zinc chloride resist process is as follows:—The goods, printed in the usual manner with resist colours, consisting essentially of zinc chloride, with or without the addition of China clay, are padded on a two-bowl padding machine through a solution of the desired Sulphur colour. The box of the padding machine is constructed to contain between 75 and 100 litres, so that the printed resists are not liable to be injured by too long an immersion in the dye liquor. After squeezing out excess of liquor, the padded cloth is passed directly, without intermediate drying, through a steam box situated immediately behind the padding machine. Any sort of a closed chamber fitted with top and bottom guide rollers is suitable for steaming purposes so long as it is large enough to allow of the pieces being steamed for 4–6 minutes. The presence of air in the steaming apparatus is an undoubted advantage, and must be provided for if the best use of the dyestuff is to be made. Usually an ordinary ager fulfils all the conditions required for steaming Sulphur colours, but in many works equally satisfactory results are obtained in simple wooden steaming boxes, furnished with guide rollers and a good supply of low-pressure steam: the necessary amount of air enters the chamber by way of the slit through which the cloth itself enters. The printed and padded cloth, after steaming, is rinsed in water, soured in dilute hydrochloric acid, washed, soaped, washed again, and dried. The process is simple and, when carried out with reasonable care, reliable. The two main points to observe are, that the cloth must pass through the dye liquor in the full open width, and that a sufficient steaming must be given to develop fully the colour before the goods are soured; creases in the cloth and too short a run through the steamer are the most fruitful causes of uneven dyeing.

The following recipes for resist colours and dye baths will illustrate the importance of the process described above. The fact that so many groups of dyestuffs are applicable is in itself sufficient to prove that the zinc chloride process offers many advantages over those hitherto employed for similar but less comprehensive classes of resist work.

Resist White Z.N.

{200 grms. British gum.
{250 „ water.
{400 „ zinc chloride.
{150 „ water.

1000

White Resist X.

{100 grms. China clay.
{100 „ water.
600 „ zinc chloride.
200 „ gum solution 1 : 2.
4 „ Ultramarine.
10 „ turpentine.

1014

Heat till the gum and salt are dissolved.

If the resist white is found to run when printed with heavily engraved rollers, it may be improved by the addition of 75 to 100 grms. China clay per kilogramme of colour: as a rule, however, this addition is not necessary with ordinary patterns.

For fast red, pink, claret, and orange resists, the Azoic colours developed on the fibre lend themselves admirably.

Resist Red Z.P.

{450 grms. 6 per cent. tragacanth thickening.
{200 „ zinc chloride.
{165 „ China clay paste 50 per cent.
{15 „ oxalic acid.

Dissolve, cool to 0° C., and add—

150 grms. diazo solution P.
20 „ acetate of soda.

1000

Diazo Solution P.

{100 grms. paranitraniline.
{55 „ nitrite of soda.
{350 „ ice and water.

Stir well together, and add—

{240 grms. hydrochloric acid 30° Tw.
{170 „ ice.

Make up to 1 litre with ice water.

For claret, pink, and orange, take the diazo solutions of α-naphthylamine, Azo rose B.B., and metanitraniline, respectively, in place of p-nitraniline.

It is almost needless to say that all Azoic colours should be printed on cloth prepared in β-naphthol or Naphthol A.S.

Fast blue, violet, and green or olive resists are best obtained from such Mordant colours as will withstand the action of the alkali in the dye bath. Of these Modern blue, Modern violet, the Chrome blues and violets for printing, Modern yellow, Anthracene yellow, and Persian berries extract are the most generally useful.

MORDANT COLOUR RESISTS (UNDER SULPHIDE COLOURS).

	BLUE.	VIOLET.	YELLOW.	GREEN.	GREY.
Chrome blue F.	50	..	..	20	..
Chrome violet M.	..	50	..	..	..
Anthracene yellow B.N.	..	..	40	40	..
Modern violet 40 per cent.	..	..	..	..	20
Persian berries extract 52½° Tw	..	..	..	..	30
Water.	300	300	310	300	320
China clay paste 50 per cent.	150	150	150	150	150
Formic acid.	20	20	..	10	..
British gum, dry	200	200	200	200	200
Dissolve, cool, and add—					
Acetate of chrome 32° Tw.	100	100	100	100	100
Zinc chloride solution 75 per cent.	180	180	200	180	180
	1000	1000	1000	1000	1000

Other colours of the same groups may be applied according to the above directions.

The basic Aniline colours are likewise suitable for the production of resist effects, but they demand more careful handling, and, though brighter, are neither so fast nor so reliable in working as the Azoic and Mordant colours.

TYPE OF BASIC COLOUR RESIST.

30	grms.	dyestuff.
70	,,	acetic acid 9° Tw.
50	,,	Acetin.
100	,,	water.
200	,,	British gum.
100	,,	water.
150	,,	China clay 50 per cent. paste. Boil, cool, and add—
150	,,	tannin solution 50 per cent. (in acetic acid).
150	,,	zinc chloride solution 75 per cent.
1000		

Victoria blue is one of the best Basic colours for the purpose; its tannin lake resists the action of alkali very well; and though converted into a brown, it is re-developed again on washing and souring.

When the Mordant and Basic colours are used, either alone or in combination with the Azoic colours, the printed goods are steamed in the rapid ager before dyeing, in order to fix their colour lakes on the fibre. In other respects they are treated exactly like the Azoic colours.

As already noted, the dyeing of the printed pieces may be carried out by either of the two methods in general use, namely,—

(*a*) With sodium sulphide and the ordinary Sulphur dyestuffs, or—

(*b*) With pure soluble Sulphur colours, and caustic soda and glucose.

(*a*) SODIUM SULPHIDE PROCESS.

The dyeing of the material is effected by padding *once* through a solution of the dyestuff in sulphide of soda and soda-ash, with or without the addition of Turkey-red oil. The concentration of the dye bath varies with the depth of

shade required. As a rule, the following proportions may be taken as representing a typical dye bath :—

Light.		Dark.		
10	to	60	grms.	Immedial or other suitable Sulphur colour.
15	to	90	,,	sodium sulphide crystals.
20	to	25	,,	soda-ash.
4	to	5	,,	Turkey-red oil 25 per cent.
To 1000	to	1000	,,	with water.

Light shades are usually padded in the cold, whereas in the case of dark shades better levelling and a fuller colour are obtained by keeping the dye bath at a temperature of between 50° and 60° C. After dyeing, the goods are steamed, rinsed, soured in dilute acid, washed, and soaped.

Example:—

1. Print White reserve X. and Red reserve N.A. on mercerised cloth prepared in a 2½ per cent. solution of β-naphthol.

Red Reserve N.A.

830	grms.	Thickening R.S.
110	,,	diazo solution (120 grms. per litre Azo rose N.A.—*p*-nitro-*o*-anisidine).
22	,,	acetate of soda.
38	,,	tragacanth thickening 60 : 1000.
1000		

Thickening R.S.

400	grms.	China clay.
400	,,	water.
1400	,,	zinc chloride.
1200	,,	tragacanth thickening 60 : 1000.
3400		

2. Dry well and slop-pad through the following dye bath :—

50	grms.	Thiogene green G.L. extra.
60	,,	sodium sulphide.
30	,,	soda ash.
860	,,	water.
1000		

3. The goods emerging from the dye bath are passed over a series of rollers for re-oxidising purposes, and then, immediately, through an open-width continuous washing machine, from which, passing through a pot-eye, they are run, in the rope form, through weak sulphuric acid (20–30 c.c. H_2SO_4 168° Tw. per litre), and are finally washed and dried. As a rule it is preferable to steam the damp padded goods for a few minutes before the first open-width wash as described under the Glucose-alkali process.

The upper roller of the padding machine is best made of rubber, and the lower of iron. The run of the goods through the machine is so arranged as to allow of the printed side being in contact with the lower roller, which is furnished with a doctor for the purpose of freeing it from any of the resist

which may stick to it. Such resist, if allowed to remain on the roller, would be transferred to succeeding lengths of cloth passing through the machine, and would result in the defect known as "marking off."

The temperature of the dye bath may vary between 50° and 90° C. according to its concentration.

(b) Glucose-Alkali Process.

The number of Sulphur colours that are soluble in caustic soda without the addition of sodium sulphide is limited, but in view of the fact that such colours are applicable by the glucose-alkali method of dyeing, they are generally preferred, where possible, to those that require dyeing by the more sensitive sulphide method.

The "soluble" Immedial colours (Cassella) are especially suitable for working with caustic soda and glucose; and although many of the pure Sulphur colours made by other firms give equally good results, the Immedial colours "soluble" are perhaps the best known in this connection. They are dyed in exactly the same manner as the ordinary Sulphur colours, the only difference between the methods being in the preparation of the dye bath, which is made up as follows:—

Light.		Dark.		
10	to	60	grms.	soluble Immedial colour.
10	to	60	,,	caustic soda 77° Tw.
20	to	40	,,	soda-ash.
10	to	60	,,	glucose.
4	to	5	,,	Turkey-red oil.
To 1000	to	1000	,,	with water.

Pad, squeeze, steam 4–6 minutes, rinse in cold water, sour in dilute hydrochloric acid ($\frac{1}{4}$°–$\frac{1}{2}$° Tw.), wash, soap well, wash thoroughly, and dry.

The sketch opposite (fig. 86) illustrates the general disposition of the plant employed in the dyeing of printed goods with Sulphur colours.

The various zinc chloride resist colours given above serve equally as resists for cover patterns printed in Sulphur colours. In this style the cloth is first printed as usual with the resists, and then, after well drying, instead of padding in the dye bath, it is over-printed or covered with a second pattern in a Sulphur colour, and finally steamed for 4–5 minutes, washed, soured, soaped, washed, and dried. In this way it is possible to obtain many novel and fast effects in coloured patterns on patterned grounds—effects that are otherwise unobtainable.

A further and very interesting and valuable property of zinc chloride is its power of effectually preventing the fixation on the fibre of many of the Vat dyestuffs.

For the production of resist styles with these colours the cloth may be treated in exactly the same way as for Sulphur colour resist styles, but the Vat dyestuffs in general are only suitable for light ground colours when dyed on the padding machine; hence they are used chiefly for classes of work analogous to the well-known cover and pad style, in which a pattern in white and a dark colour appears on a lighter coloured ground. The white resist consists of zinc chloride, while the dark colour may be obtained from either a Sulphur colour, a Vat dyestuff, a zinc chloride resist colour, Aniline-diphenyl black or Azoic black. The lighter ground, similarly, may be either a Sulphur or a Vat dyestuff, or a mixture of the two. If, for example, a two-blue and white effect with

Ciba colours is desired, the cloth is first printed with a dark Ciba blue and a zinc chloride resist white, well dried, and then, if for padding, steamed in the rapid ager, and aired to fix the dark blue. Hereupon the goods are passed through a weaker Ciba blue dye bath in the padding machine, and finally steamed in the wet state, exactly as for Sulphur colours. On the other hand, if the goods are intended for covering with another pattern, the steaming after the first printing may be omitted, since there is no likelihood of the darker blue running during the second printing into the weaker colour. After the second or cover printing the goods are dried, and then steamed in the ager for 3–4 minutes,

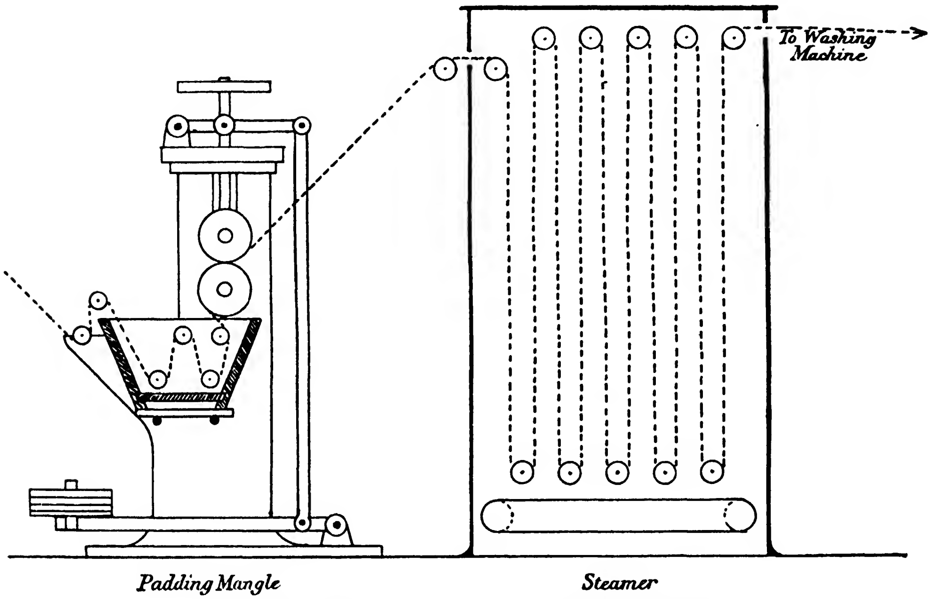
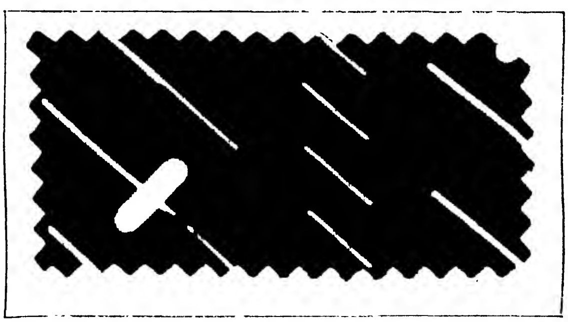


FIG. 86.—Mangle for Sulphide and Vat resist styles.

washed, soured, soaped, washed, and dried. Aniline or Diphenyl black must always be steamed after the *first* printing, otherwise its development would be prevented by the alkalinity of the covering colour.

Ciba blue may be replaced in the above style by Ciba violet, the various Indanthrene and Caledon colours, Thio-indigo red, Brom-indigos, the Algole series, etc. ; and as one of these may be used in the first printing and another in the second printing, or the dyeing, it is obvious that the process is capable of yielding a vast variety of styles.



White and Red Resists under Indigo M.L.B./4 B. (I.G.).

An illustration of the excellent effects obtained by reserving vat dyestuffs with zinc chloride is afforded by the pattern here shown—red and white under a brominated indigo.

The details of the process employed for its production are as follows :—

NAPHTHOL PREPARE.

25	grms.	β-naphthol.
25	c.c.	caustic soda 76° Tw.
40	grms.	oleine 50 per cent.
900	,,	water: make up to—
1000	c.c.	

WHITE RESIST PASTE.

460	grms.	gum Senegal 50 per cent.
80	,,	China clay 50 per cent. paste.
400	,,	zinc chloride (cryst.).

Dissolve, cool, and add—

20	grms.	anthraquinone 30 per cent.
20	,,	Leucotrope O.
20	,,	olive oil.
1000		

RED RESIST PASTE.

430	grms.	acid starch-tragacanth paste.
350	,,	zinc chloride (cryst.).

Dissolve, cool, and add—

20	grms.	anthraquinone 30 per cent.
20	,,	Leucotrope O.
20	,,	olive oil.
160	c.c.	diazo solution N.A.
1000		

DIAZO SOLUTION N.A.

168	grms.	Azo rose N.A. (*p*-nitro-*o*-anisidine).
300	c.c.	water.
300	,,	hydrochloric acid 36° Tw.
500	grms.	ice.
75	,,	sodium nitrite.
200	c.c.	water: make up to—
1600	c.c.	

The cloth is first prepared in the β-naphthol solution, then dried and printed with the white and red resist colours. After drying again, it is slop-padded in a mangle through the following dye bath :—

DYE BATH.

8	kilos.	Indigo M.L.B./4 B. paste.
4	litres	caustic soda 76° Tw.
1·6	,,	oleine 50 per cent.
1·6	kilos.	hydrosulphite conc. ($Na_2S_2O_4$), the whole made up with water to—
100 litres		

Feed Liquor for above (per 100 litres).

10 kilos. Indigo M.L.B./4 B.
4 litres caustic soda 76° Tw.
2·6 ,, oleine 50 per cent.
2 kilos. hydrosulphite conc.

100 litres

The temperature of the dye bath is maintained at about 140° F., and the pressure of the mangle bowls is adjusted to allow of the cloth absorbing about its own weight of liquor. The feed liquor is best added continuously, and across the full width of the cloth, through a perforated pipe. After padding, the goods are passed over a series of rollers to re-oxidise the dyestuff, then washed, warm soured, washed again, and finally soaped for 10 minutes in the rope form.

Another method of producing resist effects under Sulphur colours and various Vat dyestuffs was patented by the Badische Co. in 1909. It depends upon the oxidising action of manganic salts or manganese dioxide, and is applicable to the Indanthrenes, Thio-indigo, Indigo, Ciba colours, and Sulphur colours. It consists in printing the cloth with a mixture of a soluble manganous salt and an oxidising agent such as bichromate of soda, and then, after drying the material, dyeing it in one of the above-mentioned colours, according to any convenient method. Coloured resists can be obtained by adding diazo compounds to the white resist, and printing on naphthol-prepared cloth. During the drying after printing, Manganese bronze is formed, and both by its mechanical and oxidising action it effectively prevents the fixation of the colour subsequently applied in the dye vat. Manganese bronze is very fast, a feature which allows of the material being dyed at any desired temperature and in any desired manner, whether it be in the padding machine, the continuous dyeing machine, or in the dipping vat.

White Resist M.N.

{500 grms. manganous chloride.
{350 ,, 50 per cent. gum Senegal solution.

Dissolve, and add—

{ 75 grms. China clay.
{ 50 ,, water.
25 ,, bichromate of soda (ground).

1000

Red Resist M.N.

850 grms. White resist M.N.
150 ,, diazo solution M. (Paranitraniline).
30 ,, acetate of soda.

1030

Diazo Solution M.

{ 69 grms. paranitraniline.
{175 ,, hot water.
{175 ,, hydrochloric acid 32 per cent.

Cool and add—

200	grms.	ice, and then—
38	„	sodium nitrite.
200	„	ice.
143	„	water.
1000		

A 10 per cent. diazo solution is better than the above.

Similarly, α-naphthylamine may be employed for a fast claret and any of the Naphthol A.S. combinations for additional shades of yellow, orange, red, etc.

Print the colour resists on naphtholated cloth, and the white resist on the same or unprepared cloth, according to circumstances. After printing, the cloth is well dried, dyed in Indigo, etc., etc., well washed, and finally treated in an acid bath containing 10–20 c.c. sulphuric acid 168° Tw. per litre to remove the manganese salts still remaining on the fibre. Most of the Manganese bronze is reduced during the dyeing, but if any remain it may be readily removed by the addition of 2–5 grms. of potassium sulphocyanide per litre of the acid bath ; or a solution of bisulphite of soda may be used. Wash the goods again, soap, wash, and dry up.

Resists under Grounds of Padded Indigosols.

The Indigosols (soluble esters of leuco Vat dyestuffs) are readily applied, in the form of neutral or faintly alkaline solutions, to the padding of cotton and other fabrics, and are subsequently converted to the parent dyestuffs by hydrolysis and acid oxidation on the fibre. In this latter respect their mode of formation is analogous to that of Aniline black and, similarly, they may easily be resisted, *before oxidation*, by means of alkalies, alkali salts of volatile organic acids, reducing agents, metallic oxides, or insoluble carbonates—in short, by anything which will remove acids or oxygen from the *locus* of the developing reactions.

White resists are best obtained from sodium acetate, sodium thiosulphate, potassium sulphite or Rongalite C., according to the method of oxidation adopted. Rongalite C. is best adapted for wet developing processes ; the others are usually preferred for steam oxidation processes because, being non-volatile, they do not evolve reducing gases in the rapid ager—gases which retard oxidation of the ground shade and, thus, lead to irregular results.

For coloured resists it is possible to use most of the resists employed for Aniline black styles, but, in view of the excellent fastness of Indigosol grounds, only such fast dyestuffs as the Vat, Rapidogen, Rapid Fast, certain Chrome mordant colours, and the Naphtholates of the A.S. series come into practical consideration for the purpose. The much looser Basic dyestuffs are certainly applicable also, but their use is quite unnecessary and, in any case, it is rank bad practice to associate fast and loose colours in the same print, unless the required effect cannot otherwise be obtained.

The outstanding advantage of employing the Indigosols for ground colours in resist styles is that they furnish a complete range of *light and medium shades* which are easily resistible and, at the same time, of *good all-round fastness*. Such a combination of properties, in equal variety, is not attainable by any other method of resist or discharge printing. Dark grounds can also

be obtained without difficulty, but, except for exclusive styles, the relatively high cost of Indigosols renders them commercially prohibitive—moreover, dark shades of satisfactory fastness may be dyed with colours less expensive than the Indigosols. It is mainly in respect of light and medium shades that complaints regarding fastness are most frequently received.

Vat Colour Resists under Indigosols.

The chief trouble encountered in the production of Vat colour discharges on Vat colour grounds is the difficulty of preserving the discharge colours whilst the discharged ground is being removed. All Vat dyestuffs in the reduced state, and combined with Leucotrope, are more or less soluble in hot alkaline solutions, and as a hot alkaline treatment is essential to destroy or wash out the reduced ground shade, it is inevitable that a portion of the more resistant coloured discharge should be removed along with it. The success of the process depends entirely upon the difference between the alkali solubilities of ground and discharge colours and, in the case of grounds which are difficult to destroy and require considerable additions of reducing agent and Leucotrope to the discharge colours and a strong alkaline after-treatment, it is a delicate and expensive process to work. In such cases the amount of dyestuff it is necessary to use in order to obtain a satisfactory coloured discharge is often excessive and makes the process very costly.

The introduction of a complete range of Indigosols has resolved these difficulties in a manner as simple as it is elegant. By means of a simple resist process it is now possible to produce, in greater variety than hitherto and with ease and certainty, all the effects of Vat colour discharges on Vat colour grounds, in colours which, when completely developed, are themselves veritable Vat colours of standard type. Furthermore, the process is economical in that the quantity of Vat dyestuff required to give a full coloured discharge on any ground is no more than is required for ordinary white ground printing. Full dark grounds can also be resisted with equal facility although, for reasons given, they are rarely employed.

For the production of Vat colour resists under Indigosols, either the steam or the nitrite process of development may be employed. The steam process is the more generally used ; it is convenient and applicable to a wider range of ground shades than the nitrite process, which is limited, more or less, to the most easily oxidisable Indigosols, viz. those which can be fully developed in the cold. Other Indigosols require a hot acid passage for their development which, in conjunction with the free nitrous acid liberated, is more than liable to cause over-oxidation of some of the resist colours, particularly Caledon and Indanthrene blues, which may be affected beyond recovery.

(*a*) Steaming Process.—In this process, for which only the fastest Indigosols are used, it is necessary to employ an excess of oxidising agents in order to avoid as far as possible the formation of halos around the printed objects. This is only possible in the case of light grounds, a precipitation of dyestuff taking place if correspondingly large quantities of oxidising agents are added to strong solutions of Indigosols. Indigosol O. 4 B. is an exception to this rule and, being cheap, it may be used for medium and dark grounds.

Not all Indigosols are equally suitable for the steaming process of development. Only those should be chosen which are quickly and readily oxidised, that is to say, those whose development is complete before the reducing vapours, liberated in the rapid ager from the Rongalite content of the printed Vat colour resists, have time to exercise a restraining action on the oxidation.

Of the Indigosols which are unaffected or, at least, very little affected, by these reducing gases in the ager, the following are the most useful in resist styles :—

Indigosol golden yellow I.G.K.	Indigosol orange H.R.
,, scarlet I.B.	,, pink I.R.
,, green A.B.	,, brown I.R.R.D.
,, printing blue I.G.G.	,, printing purple I.R.
,, ,, ,, I.B.	,, O. 4 B.
Indigosol O.	

The preparation of the padding liquors follows closely on the lines of that of direct printing colours, except that larger proportions of oxidising agents are used and the acid-yielding component is confined to oxalate of ammonia, which is less liable to give halos than the sulphocyanide. For Indigosol green A. B. and Indigosol brown I.R.R.D., it is essential to employ diethyl tartrate (Developer D.) in place of oxalate of ammonia which precipitates the colouring matter. In all cases it is important to use a large excess of these materials in order to accelerate the development of the ground shades ; the quicker the development the less the tendency to formation of halos and the more regular the ground shade. Quick development is determined also to a great extent by the conditions under which the printed goods are steamed in the rapid ager. A copious supply of fairly dry steam in the ager is necessary for the purpose of driving out the reducing gases liberated from the printed resists during the running of the pieces in bulk. If this precaution is not observed, a progressive diminution in depth of shade is to be expected from beginning to end of the run—a defect most prevalent in the more difficultly oxidisable colours, notably Indigosol O. 4 B.

With regard to the preparation of the resist printing colours, little need be said. As a rule the Vat colours used for direct printing on white grounds are equally applicable to the production of resists under Indigosols, provided that they are made up according to the usual Rongalite-potash formulæ. Caustic soda colours are inadmissible for these styles. It is advisable to reduce the Rongalite content of the resist colours to a point as low as is consistent with proper fixation of the Vat dyestuff and, also, to keep the glycerine as low as possible, or leave it out altogether. Generally speaking, most Rongalite-potash recipes conform to these conditions and may be used without modification.

Padding liquors of the varying strengths most commonly in use are prepared according to the following general formula :—

Padding Liquors.

{ Indigosol dyestuff	2–10	grms.
{ Glyecine A.	20	,,
{ Hot water	748–710	,,
Tragacanth mucilage 60 : 1000	50	,,
Sodium chlorate 25 per cent. solution	20–30	,,
Ammonium oxalate 1 : 30	125–150	,,
Ammonium vanadate 1 per cent.	10–20	,,
Ammonia 20 per cent.	5	,,
	Make up to 1 litre	

This formula is suitable for all the aforementioned Indigosols except the

Brown I.R.R.D., Green A.B., and Orange H.R., which are not so soluble and are made up by slightly different methods :—

	Brown.	Green.	Orange.
	grms.	grms.	grms.
Indigosol brown I.R.R.D.	2–10	..	..
,, green A.B.	..	2–10	..
,, orange H.R.	..	..	3–15
Fibrit D.	20–40	..	..
Glyecine A.	..	20	20
Dissolving salt B.	..	..	2–5
Indigosol developer D.	15–20	10–15	..
Hot water		A sufficiency.	
Tragacanth mucilage	50	50	50
Ammonium oxalate 1 : 30	..	..	130–200
Sodium chlorate 25 per cent. solution	25	6–10	20
Ammonium vanadate 1 per cent.	30	30	10
Ammonia 20 per cent.	5	5	5
		To 1 litre each.	

(D. & H.)

GROUND: Indigosol Printing Blue I.G.G., 5 grms. per litre.

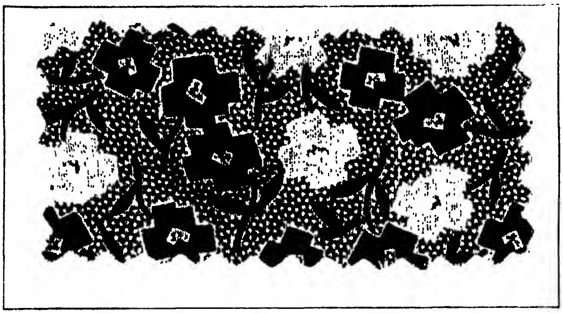
RESIST COLOURS: Indanthrene Golden Yellow G.K.; Hydron Scarlet B.B.; Caledon Jade Green.; Indocarbon C.L.

The process is carried out as follows:—(1) Pad with Indigosol solution straight through the nip of a two-bowl padding mangle, so as to avoid exhaustion of the bath ; dry in the hot-flue or over cylinders and cool the cloth before winding on for printing. (2) Print the Vat colour resists, dry well and avoid exposure to acid fumes or strong light. (3) Steam for 8 minutes in the rapid ager at 214°–216° F. with a good volume of steam. (4) Pass through a bath of bichromate of soda (2–5 grms. per litre) at 100° F. Finally wash, soap at the boil, wash, and dry.

If the print includes a white resist it is advisable to give the goods a run through caustic soda, $1\frac{1}{2}$° Tw., at the boil, before the final soaping, in order to remove all traces of undeveloped Indigosols from under the printed reserves.

An alternative to this method of working is to print the Vat colour resists on *white* cloth and then, after well drying, to over-print, with a pad or cover roller, an Indigosol steam colour prepared according to the methods described in an earlier section. The goods are then steamed, chromed, and soaped in the customary manner. The next pattern illustrates this procedure. It has

been first printed with the same Vat resists as used in the preceding pattern and afterwards " covered " in a steam developed Indigosol O. 4 B.



Vat Colour Resists under a Printed Cover of Indigosol O. 4 B. (D. & H.).

A plain pad roller may be substituted for the cover roller, or both may be used as in the " cover and pad style " for producing a variety of patterned grounds.

(*b*) THE NITRITE PROCESS.—The advantage of this process is that it permits of darker shades being padded, since precipitation of the dyestuff is less liable to occur than when the steam process is used. On the other hand, for reasons already noted, it is more limited in application, only a selected number of the more easily oxidisable Indigosols being available for multicolour resist work.

GENERAL FORMULÆ FOR NITRITE PADDING LIQUORS.

	A.	*B.*	*C.*
Indigosol dyestuff	5 grms.	10 grms.	15 grms.
Hot water	150 ,,	150 ,,	200 ,,
Soda-ash	1 ,,	1 ,,	1 ,,
Neutral tragacanth mucilage . .	50 ,,	50 ,,	50 ,,
Sodium nitrite 20 per cent. solution .	50 ,,	60 ,,	75 ,,
Nekal B.X. 10 per cent. (optional) .	10 ,,	10 ,,	10 ,,
Cold water	700 ,,	700 ,,	640 ,,
Make up to	1 litre each.		

Pad the cloth with any of these solutions, dry in the hot flue or over cylinders, print the Vat resists, steam twice for 4 minutes to fix the latter, and then develop the Indigosol grounds by a passage of 2–3 seconds through a bath of—

$$\left\{\begin{array}{l}\text{20 c.c. sulphuric acid 168° Tw.}\\ \text{1000 ,, water}\end{array}\right\}\text{at 150°–165° F.}$$

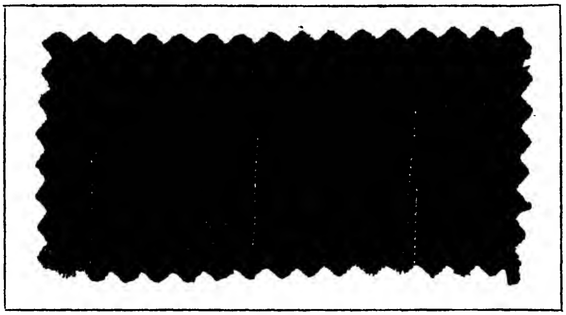
The temperature must not be allowed to fall below 150° F., otherwise the development will be incomplete. After running through the hot acid bath, the goods are given an air run of about ½ minute to complete the development, and are then washed and soaped at the boil as usual.

By this method the formation of halos is practically eliminated.

For Indigosols which are not readily dissolved at more than 10 grms. per litre, an addition of Fibrit D., Glyecine A., or Dissolving Salt B. is recommended.

Naphthol A.S. Resists on Indigosol Pads.

This process is identical with that described in detail under "Naphthol A.S. Resists on Aniline Black Pads," except that Indigosol grounds take the place of Aniline black. One example will suffice to illustrate its application, and, at the same time, show how the Naphthols may be associated with Vat dyestuffs for multicolour patterns.



(I.G.)

Ground of Indigosol O. 4 B., resisted with Naphthol A.S. and Indanthrenes, and developed in Fast Scarlet T.R. base.

(1) Pad in :—

55	grms.	Indigosol O. 4 B.
3	,,	Indigosol pink I.R. extra.
700	,,	water.
10	,,	ammonia 25 per cent.
50	,,	tragacanth mucilage.
30	,,	ammonium oxalate powder.
60	,,	sodium chlorate 1 : 2.
65	,,	ammonium vanadate 1 : 1000.

Make up to 1 litre.

Dry in the hot flue.

(2) Print the following yellow and red :—

Yellow Resist.

110	grms.	Indanthrene yellow G. double paste fine.
40	,,	Indanthrene brown R. paste.
40	,,	glycerine.
590	,,	gum arabic thickening 1 : 1.
110	,,	sodium bicarbonate.
110	,,	Rongalite C. (powdered).
1000		

Scarlet Resist (Naphthol A.S.).

150	grms.	zinc oxide 50 per cent. paste.
400	,,	thick starch-tragacanth paste.
100	,,	water.
70	,,	caustic soda 90° Tw.

Mix and stir in a solution of—

40	grms.	Naphthol A.S.
30	,,	methylated spirit.
30	,,	caustic soda 90° Tw.
150	,,	warm water.

Keep cool and add—

30 grms. caustic soda 90° Tw.

1000

(3) After printing, dry, steam for 5 minutes, and then develop in a diazo solution of—

Scarlet Developer (for padding machine).

30	grms.	Fast Scarlet T.R. base.
500	c.c.	cold water.
30	,,	hydrochloric acid 32° Tw.
12	grms.	sodium nitrite.
50	c.c.	cold water.

Allow to stand for 20 minutes, then filter and add—

23	grms.	sodium acetate.
80	c.c.	water.

Make up to 1000 c.c.

On emerging from the developing solution the goods are given a short air passage of about one minute over rollers, to complete the coupling, then squeezed between the mangle bowls and, finally, washed and soaped at the boil, etc., as usual.

For further details and additional Naphthol A.S. combinations suitable for Resists, the reader is referred to the corresponding Aniline black style.

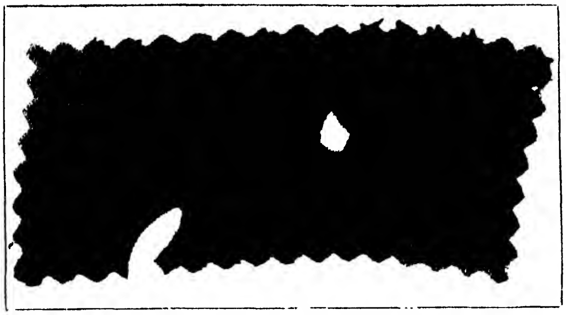
Rapid Fast and Rapidogen Colour Resists under Indigosol Pads.

Here again there is a close relationship between the Indigosol and Aniline black styles, so much so, in fact, that in many cases it is possible to use exactly the same Resist colours under both types of grounds.

The Rapid Fast and Rapidogen dyestuffs are particularly well adapted to the production of brilliant and fast resist effects on Indigosol-padded grounds of various shades and depths. The Rapid Fast colours are applied by the steaming method of development, whereas the Rapidogens are applicable by several variations of both steaming and nitrite processes. Gaps in both ranges may be filled by the use of Vat and certain Chrome colours.

Rapid Fast Colour Resists.—In this process the goods are padded with Indigosols, prepared according to the steaming recipes, and then printed with Rapid Fast colours and Rapidogen G. combinations containing acetate or thiosulphate of soda as resisting agent. Development of both ground and resists is effected by a short steaming, followed by a passage through dilute acetic acid (to brighten the resist colours), washing and soaping.

If Vat colours form part of the colouring scheme, the steamed goods are treated in a warm acidified bath of perborate of soda before washing and soaping.



Vat and Rapid Fast Colour Resists under Indigosol Ground (Mixture) (I.G.).

The pattern shown is typical of the style and may be reproduced by working according to the following method and formulæ:—

(1) Pad the bleached goods with an Indigosol blue padding liquor in a 3-bowl mangle:

BLUE PADDING LIQUOR.

40	grms.	Indigosol O. 4 B.
20	,,	Indigosol violet A.Z.B.
600	c.c.	water.
30	grms.	tragacanth mucilage 65 : 1000.
60	c.c.	sodium chlorate 1 : 2 solution.
15	grms.	ammonium oxalate (crys.).
140	c.c.	warm water.
75	,,	ammonium vanadate solution 1 : 1000.
10	,,	ammonia 25 per cent.

Make up to 1 litre

Dry in the hot flue at about 120° F.

(2) Print the following resist colours as soon as possible:—

WHITE RESIST.

500	grms.	British gum thickening 1 : 1.
75	,,	Rongalite C. powdered.
75	,,	water.
50	,,	Leucotrope W. conc.
100	,,	zinc oxide 50 per cent. paste.
150	,,	sodium acetate.
50	,,	water or thickening.
1000		

RED RESIST.

100	grms.	Rapid Fast red R.H. paste.
150	,,	Rapid Fast scarlet L.H. paste.
25	,,	Monopol Brilliant Oil.
60	,,	water at 75°–85° F.
13	,,	caustic soda 62° Tw.
550	,,	neutral starch-tragacanth paste.
70	,,	sodium thiosulphate.
30	,,	cold water.
To 1000		

YELLOW RESIST.

60 grms.	Naphthol A.S.-G.
30 ,,	Monopol Brilliant Oil.
15 ,,	caustic soda 62° Tw.
150 ,,	Rapidogen G. paste, double conc.
205 ,,	water at 75°–85° F.
450 ,,	neutral starch-tragacanth paste.
60 ,,	sodium thiosulphate.
30 ,,	sodium acetate.
1000	

GREEN RESIST.

150 grms.	Indanthrene brilliant green 4 G. double paste fine.
30 ,,	glycerine.
20 ,,	Dissolving Salt B. 1 : 1.
490 ,,	B.W.S. thickening (see below).
75 ,,	potassium carbonate.
120 ,,	Rongalite C.
65 ,,	water.
50 ,,	potassium sulphite 90° Tw.
1000	

B.W.S. THICKENING.

600 grms.	water.
100 ,,	wheat starch.
20 ,,	Dissolving Salt B.
280 ,,	British gum (dry).
1000	

Boil and cool.

(3) After printing and drying in hot air at a moderate temperature, the goods are steamed for 3–5 minutes in the rapid ager with fairly moist steam at 214°–216° F., then passed, in the open width, through a warm bath of—

1 grm.	sodium perborate	at 75° F.
2 c.c.	acetic acid 50 per cent.	
1000 ,,	water	

to reoxidise the Vat colour green; finally the goods are thoroughly washed and soaped for 8–10 minutes at 200°–212° F. in an alkaline soap bath (containing ½–1 c.c. caustic soda, 62° Tw., and 3 grms. soap per litre), then washed again and dried.

Other Indigosols, Vat colours, and Rapid Fast reds or oranges may be employed in the same manner, more or less, as those just instanced.

Rapidogen Colour Resists.—For the production of coloured resists on Indigosol grounds, the Rapidogen dyestuffs are superior to the Rapid Fast colours and also to those obtained by printing thickened Naphtholates of the A.S. series. The printing pastes are stable, the shades are brighter, a wider range of colours is available, including a fine yellow and a useful green, and either steam or nitrite methods of developing the grounds may be employed, as occasion dictates, so that altogether the Rapidogens offer considerable advantages over other Azoic colours for the style in question.

I. Steam Processes.—By suitable adjustment of formulæ these processes may be arranged to allow of the development of the Indigosol grounds and Resist colours, respectively, being carried out either (*a*) separately or (*b*) simultaneously.

In the first case, (*a*), the grounds are padded according to the usual steaming process formulæ, printed with the Rapidogen resists, steamed (to develop the Indigosol ground), and finally passed through a hot acid bath in order to develop the Resist colours.

In the second case, (*b*), the acid bath is omitted, the acid necessary for the full development of the Rapidogen resists being furnished by the Indigosol padding liquor itself, to which an excess of acid-yielding salts is added—salts which split off free acid during steaming.

Light Indigosol grounds (1 to 6 grms. dyestuff per litre) are very easily reserved by slightly alkaline printing mixtures, and excellent resist effects can be obtained by using ordinary Rapidogen printing colours as made up for white ground printing. Such colours, however, cannot be used successfully for reserving *medium and dark* Indigosol grounds. The degree of acidity necessary for the full development of these grounds is not sufficiently high to act in like manner on the printed resist colours; nor are the latter sufficiently alkaline to prevent completely the oxidation (or development) of those portions of the Indigosol ground over which they are printed. The result is that the Rapidogen colours are partially developed over an equally partially developed part of the ground and, consequently, show up as dull and imperfect resists, which exhibit irregular patches and dark edges which no after-treatment will eradicate.

To avoid these difficulties it is only necessary—

(*a*) to augment the reserving effect of the Rapidogens and, at the same time, protect them against acid attack during the development of the grounds by adding zinc oxide and sodium thiosulphate to the Resist colours, which are, subsequently, separately developed in an acid bath; or

(*b*) to increase, in the first instance, the proportion of acidic components in the Indigosol padding liquor so that complete development of the Rapidogens takes place during steaming without interfering with their reserving action on the ground shades.

The data given in the following tables are typical of those employed in these two methods of working; they are not absolute, of course, and must be modified in detail according to the conditions under which they are applied.

(*a*) *Development of Ground by Steaming and of Resists by Acid Treatment.*—Pad the cloth in a 3-bowl mangle with Indigosols made up according to the following general recipes:—

I.

Indigosol dyestuff	7–15	grms.
Fibrit D. or Glyecine A.	20–50	,,
Hot water	300	c.c.
Neutral tragacanth thickening	50	grms.
Cold water	568–515	c.c.
Sulphocyanide of ammonia 1 : 1	10–15	grms.
Sodium chlorate 10 per cent.	30–40	,,
Ammonium vanadate 1 per cent.	10	,,
Ammonia 20 per cent.	5	,,
	1000 grms.	

II.

	1.	2.	3.
	grms.	grms.	grms.
Indigosol Brown I.R.R.D.	7–15	..	..
,, Green A.B.	..	7–15	..
,, Golden Yellow I.R.K. or I.G.K.	..	..	7–15
Fibrit D. or Glyecine A.	30–50	20–50	20–50
Indigosol Developer D.	20–30	20	20
Dissolving Salt B.[1]	7–15	..	..
Hot water	400	400	400
Neutral tragacanth thickening	30	25	25
Chlorate 10 per cent.	30–50	30–40	20–30
Ammonia 20 per cent.	..	5	5
Vanadate 1 per cent.	40	30–40	20
Nekal B.X. 10 per cent.	10	10	10
Bulk to	1000 grms.		

Dry gently in the hot flue or over not too hot cylinders and print:—

RAPIDOGEN RESISTS.

	1.	2.	3.	4.	5.	6.
	grms.	grms.	grms.	grms.	grms.	grms.
Rapidogen Red G.	80	..	..	..	..	..
,, Scarlet R.	..	80	..	..	..	..
,, Yellow G.	..	..	80	..	..	..
,, Orange G.	..	..	..	80	..	..
,, Violet B.	..	..	..	..	25	..
,, Blue B.	..	..	..	..	..	25
Water	230	230	250	230	270	270
Caustic soda 72° Tw.	50	50	20–30	50	20	20
Monopol Brilliant Oil	30	30	30	30	25	25
Neutral starch-tragacanth thickening	400	400	400	400	450	450
Zinc oxide 1 : 1	200	200	200	200	200	200
Thiosulphate crystals	10	10	20–10	10	10	10
	1000 grms.					

After printing, dry, steam for 7–8 minutes in the rapid ager to oxidise the ground, and then develop the Rapidogen resists by a 5-second run at 190°–195° F. through a bath of—

[1] A solution of sodium dibenzylsulphanilate in diethylene glycol is a far better solvent for all sulphuric esters of leuco vat dyestuffs than Dissolving Salt B. It confers good working properties on printing colours containing Indigosol brown I.R.R.D., Indigosol Pink I.R., and other leuco vat colours of low solubility. Sodium dibenzylsulphanilate is made by the Imperial Chemical Industries Ltd., and marketed as Solution Salt S.V.

25 c.c.	acetic acid 12° Tw.
10 ,,	formic acid 90 per cent.
25 grms.	sodium sulphate

To 1000 c.c. with water.

Squeeze, run in air for 30–40 seconds, wash thoroughly, and soap at the boil, again wash and dry. Any previously mentioned White resist may be used along with the foregoing colours.

(*b*) *Grounds and Resists Developed Simultaneously by Steaming.*—In this process the Rapidogens are developed by an excess of an easily dissociable acid salt added to the Indigosol padding liquor. For the purpose sulphocyanide of ammonia has been found to give good results in practice.

For medium and dark grounds the cloth may be padded, for example, in one of the following solutions:—

Indigosol Padding Liquors.

	I. grms.	II. grms.	III. grms.
Indigosol O. 4 B. .	7	15	50
Glyccine A. or Fibrit D.	..	20	40
Hot water	300	300	300
Cold water	500	500	400
Neutral tragacanth 60 : 1000	50	50	50
Sodium chlorate 10 per cent. solution	50	50	100
Ammonium sulphocyanide 50 per cent. solution	40	40	40
Ammonium vanadate 1 per cent. solution	10	10	10
Make up to	1000 grms.		

The more insoluble brands of Indigosols are better prepared as shown in the table below.

	1.	2.	3.	4.	5.	6.	7.	8.	9.
Indigosol Green A.B.	7	11	15	..	..	..	..	..	..
,, Brown I.R.R.D.	..	..	..	7	11	15	..	..	..
,, Golden Yellow I.G.K.	..	..	..	..	..	..	7	11	15
Glyccine A.	10	20	20	..	..	..	10	10	15
Dissolving Salt B.	..	..	..	15	20	30	..	..	..
Fibrit D.	..	..	..	40	40	40	10	10	10
Indigosol Developer D.	40	40	50	40	40	50	40	40	50
Water	833	819	800	788	779	750	823	819	795
Tragacanth	50	50	50	50	50	50	50	50	50
Chlorate 1 : 3	25	25	30	25	25	30	25	25	30
Vanadate 1 per cent.	30	30	30	30	30	30	30	30	30
Ammonia 20 per cent.	5	5	5	5	5	5	5	5	5
	1000 grms.								

It is not advisable to use more than 15 grms. of dyestuff per litre.

The padded goods, dried in the hot flue, are then printed with the following Rapidogen resists:—

RAPIDOGEN RESISTS.

	1. grms.	2. grms.	3. grms.	4. grms.
Rapidogen Scarlet R.	80	..	..	..
,, Orange G.	..	80	..	..
,, Yellow G.	..	..	80	..
,, Blue B.	..	..	..	45
Tepid water 30° C.	260	275	280	225
Caustic soda 72° Tw.	30	25	20	30
Neutral starch-tragacanth thickening	500	500	500	500
Alcohol	30	30	30	30
Zinc oxide 1 : 1	50	50	50	50
Sodium nitrite 20 per cent.	50	40	40	40
Glyecine A.	..	..	..	30
Urea	..	..	..	50
	1000 grms.			

After printing, steam for 8 minutes in the rapid ager, wash, soap at the boil, wash, and dry.

(*c*) A *third method* of obtaining Rapidogen resists under steam-developed Indigosol grounds consists in printing the resists on white *unpadded* cloth and afterwards applying the ground shade by padding "straight through the nip" as carried out for Aniline black resist styles. Almost any resists containing zinc oxide and sodium thiosulphate may be used for this purpose. A suitable colour, for instance, may be made by replacing the nitrite of soda, in the immediately preceding recipes, with an equal quantity of sodium thiosulphate, the rest of the ingredients remaining the same.

The white cloth printed with the resists, and dried, is padded as described with Indigosols made up according to the following general formula :—

PADDING LIQUOR.

7– 30	grms.	Indigosol dyestuff.
20– 30	,,	Fibrit D.
800–750	,,	water.
50	,,	tragacanth 60 : 1000.
20	,,	ammonium oxalate.
30	,,	ammonium acetate.
45	,,	sodium chlorate 1 : 2.
20	,,	ammonium vanadate 1 per cent. solution.

To 1000 with water.

Dry after padding, steam for 7 minutes, wash, soap at the boil, wash, and dry.

II. NITRITE PROCESSES.—Compared with the steaming processes of developing Indigosol grounds, the nitrite processes possess advantages which permit of them being employed in circumstances unfavourable to the use of the former methods. In the first place, owing to the good stability of the nitrite padding liquors, it is possible to store the padded cloth for a considerable time before printing, whereas the steaming processes require that it be printed at once; if need be, the goods may be kept in good condition for as long as a fortnight, provided they are protected from light and acid vapours. In the second place, all steaming operations are dispensed with and, consequently, no trouble is to be anticipated from those fruitful causes of defects

which take the form of drops of condensed water and over-moist steam. Moreover, by the nitrite processes no difficulty is experienced in obtaining medium and dark shades, as precipitation of the dyestuff is much less liable to occur than in the case of steam processes.

The Rapidogen printing pastes used for reserving Indigosol-Nitrite paddings require to be protected against premature partial development by the usual additions of zinc oxide and sodium thiosulphate. These additions act also as resisting agents, and effectually prevent the oxidation of any Indigosol ground colour under the printed pattern.

The printed resists and the Indigosol grounds are developed simultaneously by an acid treatment, which may be carried out in two different ways: (*a*) by padding in *cold* solutions of organic acids, followed by immediate drying over steam-heated drums (drying cylinder process), or (*b*) by a passage through hot acid solutions followed by a short airing, washing, etc. (acid bath process).

(*a*) *The Drying Cylinder Process.*—This method, introduced by the I. G. Farbenindustrie A.G., Frankfurt a/M., is carried out as follows:—

The goods are padded with Indigosol solutions prepared according to the usual nitrite recipes, but containing an excess of nitrite. Thus:—

General Recipe.

Indigosol dyestuff	5–30	grms.
Glyecine A.	0–30	,,
Water	920–865	c.c.
Tragacanth thickening 60/1000 . .	50	grms.
Sodium nitrite, dry	15	,,
Ammonia 20 per cent. . . .	10	,,
	To 1000	c.c.

Dry and print the Rapidogen resists.

Rapidogen Resists.

	1.	2.	3.	4.	5.	6.
	grms.	grms.	grms.	grms.	grms.	grms.
Rapidogen Yellow G.	80	..	..	..	..	..
,, Scarlet R.	..	80	..	..	..	..
,, Red G.	..	..	80	..	..	..
,, Red R.	..	..	..	80	..	..
,, Violet B.	..	..	..	..	30	..
,, Blue R.	..	..	..	..	..	30
Warm water at 40° C.	100	100	100	100	100	100
Alcohol	30	30	30	30	30	30
Caustic soda 72° Tw. . . .	20	30	30	30	35	30
Glyecine A.	..	..	..	..	..	50
Paste the dyestuff with a mixture of water and alcohol, caustic soda and, finally, Glyecine.						
Neutral tragacanth thickening .	500	500	500	500	500	500
Zinc oxide 1 : 1	50	50	50	50	50	50
Thiosulphate of soda . . .	50	50	50	50	50	50
Water	170	160	160	160	205	160
	1000 grms.					

After printing, dry and pad, printed side downwards, between the bowls of a 2-bowl padding mangle—the lower bowl of which is wrapped and running partly immersed in the acid bath—through a cold mixture of—

10 grms. oxalic acid,
20 c.c. formic acid 90 per cent.,
20 grms. sodium sulphate,

per 1000 c.c. of water,

and dry immediately over moderately heated cylinders, the first of which it is advisable to wrap with calico. After drying, the goods are washed, soaped at the boil, washed, and dried.

Development of the Indigosol ground takes place partly during the passage through the acid bath (wherein nitrous acid is liberated), and is completed on the drying machine, where also the Rapidogen resists, under the combined influence of heat and acid, are simultaneously fully developed.

(*b*) *Acid Bath Developing Process.*—In works where a combined padding mangle and drying machine is not available for developing Indigosol resist prints, or where, for other reasons, it is inconvenient to use the drying cylinder process, equally good results may be obtained by passing the printed goods through a *hot* acid bath for a longer period. During the passage of the cloth (impregnated with a mixture of Indigosol and nitrite of soda), the bath gradually becomes charged with a certain amount of free nitrous acid which, being both a mineral acid and an oxidising agent, tends to nullify the reserving action of the Rapidogen colours and also to inhibit, if not to prevent, their full development. If the bath becomes too active the Indigosol ground is apt to develop up under the printed resists or reserves, with disastrous effect on the brightness of the latter. This trouble does not always arise. Its occurrence is determined largely by the relation between printed resists and padded ground, by scale of engraving and depth of ground shade, and it may appear and disappear during the course of a single run of goods through an acid developing bath if the "run" happens to consist of an assortment of patterns engraved to different scales and printed on different grounds. But it is always a liability in wet developing processes unless the resist colours are adequately *buffered* against acid attack and are also capable of preventing the oxidation of the underlying ground colour. These conditions are best fulfilled by the simple means of increasing the zinc oxide and sodium thiosulphate contents of the resist colours and by reducing, as far as possible, the proportion of sodium nitrite in the Indigosol padding liquors.

The formulæ given below are representative of those in use for the production of Rapidogen resists on Indigosol grounds developed by the acid bath method.

General Recipe for Padding Liquors.

Indigosol dyestuff	2	to	15 grms.
Glyecine A.	0	,,	15 ,,
Fibrit D.	0	,,	20 ,,
Hot water	300	,,	300 ,,
Cold water	600	,,	580 ,,
Neutral tragacanth 60 : 1000	50	,,	50 ,,
Soda-ash	1	,,	1 ,,
Sodium nitrite	10	,,	10 ,,
	per		1000 c.c.

The more insoluble Indigosols (Brown I.R.R.D. and Green A.B.) require less nitrite than the above (say 6–8 grms.), and also an addition of Fixer C.D.H. (urea) to ensure a good solution. The nitrite is best added at a temperature of 120°–140° F., and it is advisable also, in the case of the darker shades, to carry out the padding at this temperature.

After padding and drying the goods are printed with:—

RAPIDOGEN RESISTS (Acid Bath Process).

	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Rapidogen Yellow G.	80	..	..	..	..	..	..
,, Orange G.	..	80	..	..	..	..	..
,, Scarlet R.	..	..	80	..	..	..	..
,, Red G.	..	..	..	80	..	..	..
,, Blue B.	..	..	..	..	30	..	..
,, Violet B.	..	..	..	..	..	30	..
,, Brown I.R.	..	..	..	..	..	..	80
Caustic soda 70° Tw.	30	30	30	30	30	30	30
Methylated spirit	30	30	30	30	..	..	30
Glyccine A.	..	..	..	..	30	30	..
Warm water	150	150	150	150	150	150	200
Mix to a smooth paste and add—							
Neutral starch-tragacanth paste	420	450	450	450	400	400	460
Zinc oxide 50 per cent. paste	200	200	200	200	300	300	150
Sodium thiosulphate crys.	90	60	60	60	60	60	50
	1000 grms. each.						

WHITE RESIST.

100 grms. zinc oxide.
100 ,, water.
150 ,, sodium acetate crys.
150 ,, sodium thiosulphate crys.
500 ,, starch-tragacanth paste.

1000

After printing and drying, the goods are developed by passing for 5 seconds, at 195° F., through a roller tank containing—

10 grms. oxalic acid,
20 c.c. formic acid 90 per cent.,
25 grms. sodium sulphate,

per 1000 c.c. (water).

after which they are squeezed, given an air passage of 30 seconds, washed, soaped at the boil, washed, and dried.

CHROME COLOUR RESISTS UNDER INDIGOSOL PADS.

The fastest and, as far as possible, the brightest chrome mordant colours, made up in the manner usual for white ground printing, may readily be con-

verted into efficient resists on Indigosol grounds by an addition of acetate or thiosulphate of soda, varying from 50 to 250 grms. per litre of colour, according to the depth of ground to be reserved. The style is confined to the steam process for Indigosol development, since Chrome colours are more or less destroyed by more drastic oxidation processes.

The goods, padded with Indigosols prepared according to any of the steaming recipes already described, are dried and printed, as soon as possible, with the Chrome colour resists. (It is important to proceed with the printing without undue delay in order to guard against premature oxidation of the ground.) After printing and drying, the goods are steamed twice for 5 minutes in the rapid ager at 214°–216° F., and then washed, soaped at 190°–200° F., and washed and dried on the open soaping range, the final operations being continuous.

An alternative and more convenient method of obtaining the same result consists of printing the Resist colours on white cloth before padding the Indigosol ground. The printed goods are steamed, in order to fix the Chrome colour resists, and may then be allowed to lie for any reasonable time before padding with the Indigosol ground colour. If desired, they may also be stored before steaming and the process completed at convenience. By working in this manner, the printing and padding operations are independent of each other, and there is no necessity to regulate the output of one machine to balance the consumption of another—an advantage of great practical value.

The printing colours are composed essentially of colouring matter, chromium acetate, Lithopone, and zinc oxide, the last-named acting as the resisting agent and, at the same time, along with Lithopone, serving to prevent the colours from running during the steaming and padding operations. The colours may all be prepared in the same manner according to the general formula below:—

Chrome Colour Resists Printed before Padding.

20– 40	grms.	colouring matter.
130– 50	,,	water.
450	,,	tragacanth mucilage 65 : 1000.
200	,,	zinc oxide 50 per cent. paste.
40	,,	urea.
100	,,	Lithopone 50 per cent. paste.
60–120	,,	chromium acetate 32° Tw.
1000		

The following colouring matters have been found to satisfy most demands for good general fastness:—

Chromocitronine R. (40).
Chrome fast xanthine 2 R. (30).
Chromorhodine B., 2 B. (40).
,, 6 G.S. extra (30).
Chrome printing red Y. (40).
Brilliant chrome blue S. (20).
,, ,, violet S. (40).
Chrome green G.D. (Bayer) (30).
Modern grey R.C. 2 N. (20).

The figures in brackets indicate grammes per kilogramme of printing colour.

Other shades may be obtained by mixing the foregoing colours or by varying the quantities of colouring matter and chromium acetate, keeping the rest of the ingredients the same.

The process is simple. The resist colours, printed on white cloth, are

first fixed and developed by steaming the goods for 45–60 minutes in an ordinary continuous steamer; they are then padded in an Indigosol colour solution made up according to the steam developing formulæ, aged for 6–8 minutes at 214°–216° F. in the rapid ager to develop the padded ground shade, and finally washed and soaped at about 195°–200° F. in the open soaping machine.

Chrome colour resists under Indigosols are somewhat inferior in all-round fastness to those obtained from Vat and Azoic dyestuffs, but they are not by any means to be regarded as loose colours. They withstand satisfactorily any ordinary washing, and are faster to light than many colours that are used in large quantities for resist and discharge styles on other types of grounds. They are also less expensive than Vat and Rapidogen dyestuffs, and permit of a sound article being produced at a relatively low cost.

Resists under Indigosol O.

Indigosol O., the first member of the Indigosol series, is, as already stated, a soluble ester of leuco-indigotin and, as such, its use in textile printing is confined chiefly to the production of standard Indigo styles. It is rarely employed in conjunction with other Indigosols, and even in its own particular province its comparatively high price limits its application more or less to special styles which are difficult or impossible to execute by means of ordinary Indigo.

Indigosol O. is readily resisted by the same alkali salts and reducing agents as are used for other brands; and all recipes given elsewhere for resisting other Indigosols are equally suitable for Indigosol O., whether printed or padded, and whether developed by the steaming, nitrite, or bichromate process.

The classic Red-Blue style, which formerly involved a previous dyeing of the cloth in Alizarin red, and also the production of coloured resist effects under printed pads and covers of Indigo, which was impracticable with Indigo itself, are both produced, with ease and certainty, by means of Indigosol O., using Vat, Rapidogen, Rapid Fast, or Chrome colours as resists. The facility, too, with which a perfect white may be obtained on Indigosol O. in these hitherto difficult styles, is a point of some importance, especially in the case of the Red-Blue article, in which a white could not previously be given except by the risky and unreliable process of printing chlorate discharges [$NaClO_3$ for white, $Al_2(ClO_3)_6$ for red] on dyed Indigo, followed by steaming, dunging, and dyeing in Alizarin.

The justifiable expectation, aroused on its introduction to the industry, that Indigosol O., with its simple methods of application, would eventually become the standard dyestuff for the production of the many and often complex Indigo specialities, has not been realised to the full—Variamine and other fast Azoic blues, of later appearance than Indigosol O., now account for much of the work that was formerly executed with Indigo, and in so far as this class of work is concerned, Indigosol O. has no future. But there are still important markets which insist on being supplied with genuine Indigo printed and dyed goods, and it is to the satisfaction of these demands that Indigosol O. is well adapted.

As Indigosol O. conforms to the general processes employed for other Indigosols, except that it is used in greater concentration for most purposes, it is not necessary to give more than one example of its application, viz. its use in the well-known Red-Blue style:—

Red-Blue Style.

(1) Pad the cloth in a 3-bowl mangle with:—

{100 grms. Indigosol O.
{600 ,, hot water.
{ 50 ,, tragacanth mucilage 60 : 1000.
{ 90 ,, water.

Mix and, when dissolved, cool and add:—

25 grms. sodium chlorate 25 per cent. solution.
40 ,, ammonium sulphocyanide 50 per cent. solution.
50 ,, ammonium vanadate 1 per cent. solution.
10 ,, ammonia 25 per cent.

Make up to 1000 c.c.

(2) Dry in the hot flue and print—

Red Resist.

{ 80 grms. Rapidogen red R.
{190 ,, water.
{ 50 ,, caustic soda 70° Tw.
{ 30 ,, methylated spirit.
400 ,, neutral starch-tragacanth paste.
180 ,, zinc oxide 1 : 1.
70 ,, sodium thiosulphate crys.

1000

(3) Dry after printing, steam for 4–5 minutes in the rapid ager to develop the Indigosol ground, then develop the Rapidogen red resist by a passage of 5 seconds through an acid bath of—

25 c.c. acetic acid 50 per cent.,
10 ,, formic acid 90 per cent.,
25 grms. sodium sulphate,

To 1000 c.c. with water,

at 190°–195° F.; squeeze, run in air for 30 seconds, wash and soap as usual.

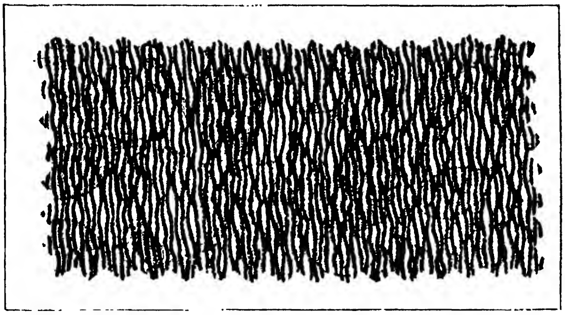
Similarly, Indigosol O. pads, according to any process, may equally well be resisted with Vat and Chrome colours made up as described under various headings in preceding pages.

Rapidogen-Indigosol Conversion Styles.

By a modification of the process described for the simultaneous development of Rapidogen resists and Indigosol padded grounds (see Rapidogen Colour Resists: Steaming Processes (*b*)) it is possible to obtain a variety of attractive conversion effects under printed covers of Indigosols. In principle the modification consists simply of printing, instead of padding, the Indigosol; and fairly satisfactory results may be obtained in this way. But much better results and clearer cut resists are produced by working on the lines of the formulæ set out opposite. The resisting action of the alkaline Rapidogen colours is reinforced by additions of zinc oxide and sodium thiosulphate, which also provide against the possibility of undesired development of the Rapidogens taking place during steaming in those parts which do not fall under the over-printed Indigosol cover pattern. On the other

hand, the Indigosol covering colour is acidified by an addition of glycollic acid in order that wherever it falls over the previously printed Rapidogens it will furnish the necessary acid for their full development during steaming. Where the Indigosol colour does not fall over the Rapidogens no development takes place, and the latter are removed from the cloth completely by subsequent washing operations.

The printed example illustrating this interesting process exhibits an all-over cover pattern of unbroken wavy lines which change in colour from blue, on the plain white ground, to red and brown as they pass over the previously printed Rapidogens. The effect is produced by printing, first, *solid* red and brown leaves in Rapidogen colours, and then, after drying, over-printing the wavy line cover in Indigosol blue. The Rapidogens are developed only in those parts of the leaves crossed by the blue, the remainder, between the lines, being unaffected and subsequently washed out.



Indigosol-Rapidogen Colour Conversion Effect (I.G.).

(1) Print on white cloth :—

RED AND BROWN RESISTS (2-Colour Leaf Pattern).

Rapidogen scarlet R.	80 grms.	..
Rapidogen brown I.B.	..	80 grms.
Methylated spirit	30 ,,	30 ,,
Caustic soda 72° Tw.	40 ,,	40 ,,
Lukewarm water	100 ,,	100 ,,
Neutral starch-tragacanth paste	350 ,,	350 ,,
Zinc oxide 50 per cent. paste	50 ,,	50 ,,
Sodium thiosulphate	30 ,,	30 ,,
Cold water (or tragacanth)	320 ,,	320 ,,
	1000	1000

(2) Dry and cover with the line pattern in :—

Indigosol printing blue I.G.G.	40 grms.
Glyecine A.	30 ,,
Water at 175° F.	415 ,,
Neutral starch-tragacanth paste	350 ,,
Ammonia 25 per cent.	30 ,,
Glycollic acid	30 ,,
Ammonium sulphocyanide	40 ,,
Sodium chlorate	15 ,,
Ammonium vanadate 1 : 1000	50 ,,
	1000

Dry and steam for 5 minutes in the rapid ager, pass through a hot dilute caustic soda solution (1 c.c. caustic soda, 72° Tw., per litre), soap at the boil with addition of 2 grms. soda-ash per litre, wash, and dry.

It is important to keep the printing colours as thin as is consistent with a sharp impression of the engraving; if too thick, their interpenetration is impeded, with the result that irregularities of shade are obtained owing to the incompleteness of the reactions.

In a similar manner it is easily possible to obtain an immense variety of conversion effects by utilising other members of the Rapidogen and Indigosol series of dyestuffs.

Indigosols in Cover Styles.

The Indigosol cover styles are merely adaptations of the various resist processes to the production of a figured or patterned ground in place of the usual plain ground, and call for no more than a brief general description.

The white cloth is first printed with any of the usual Resist colours containing an alkali or a reducing agent or both, and then, after drying (and steaming if necessary), over-printed or covered with an Indigosol colour prepared according to the steam development process. The goods are then steamed and after-treated according to the requirements of the resist colours employed.

All the resist colours used on Indigosol-padded grounds, whether made up from Vat, Rapidogen, Rapid Fast, or Chrome mordant dyestuffs, are suitable for covering with Indigosol steam colours. The amount of alkali or reducing agent in these several types of resist colours may require to be increased or diminished according to the depth of engraving or the concentration of the covering colour, but this is a simple matter, easily decided by a practical trial.

Excellent effects can also be obtained by the nitrite process of development; indeed, any process of developing the Indigosol covers may be adopted provided the resist colours will stand the treatment. Suitable colours for these methods will be found under the appropriate headings dealing with their application (*vide* Resists under Indigosol-padded Grounds).

For the printing of large patterns in yellow, orange, and red resists under heavy Indigosol covers—such patterns as are produced for the West Coast and Far East trades—it is often preferred to employ the process based on the printing of thickened naphthols (page 535). The goods are printed with a Naphtholate of the A.S. group, with or without an addition of sodium acetate, dried and over-printed with Indigosol O. or O. 4 B. (steam colour), steamed for 4–5 minutes in the rapid ager, and finally the naphthol resists are developed by a passage through a suitable diazo solution.

Indigosol Resists under Various Covers.—By reversing the process Indigosols may themselves be used as Resists under printed covers of Aniline black or Azoic, Chrome, and Vat colours.

Under Aniline black covers the Indigosol resists are the same as those used on Aniline black pads, already described. If anything, those containing zinc acetate as resisting agent give the best results in respect of shade; on the other hand, those made up with zinc oxide and a little caustic soda are less liable to run and give sharper prints as a rule. Whichever may be preferred, the process is the same. The goods are printed with the Indigosol resists, dried, covered with a fine pattern in a steam ferrocyanide Aniline black, aged for 2–3 minutes in a rapid ager to develop the black, and then passed through a bath of bichromate of potash and sulphuric acid as described for Indigosol resists under Aniline black pads (*q.v.*).

Vat colour covers may be resisted by ordinary steam Indigosol colours to which have been added 150 grms. Ludigol per kilo. of printing colour. The cloth

printed with the resists, is covered with an ordinary Rongalite-potash Vat printing colour, aged for 5–8 minutes and chromed, washed, and soaped as usual.

Chrome colour covers may be resisted similarly by means of an addition of citrate of ammonia to the usual Indigosol steam colours, the amount of citrate being determined by the depth of the Chrome colour cover to be reserved. In this case the goods, after printing and covering, are simply steamed, washed, and soaped.

Indigosol resists under Azoic colour covers, such as Variamine blue, may be obtained by methods practically identical with those used for Resists under Variamine blue pads (*q.v.*), the only difference being that the blue is printed instead of being slop-padded in a mangle. The Azoic colour covers are restricted to Variamine and Dianisidine blues on Naphthol A.S.; all others are either imperfectly resisted, or not resisted at all, by any practicable Indigosol composition.

Rapidogen and Indigosol Reserves under Padded Chrome Colour Grounds.

This process is a modern version of an older method of obtaining resist effects under steam-developed mordant colours.

The old-fashioned Trianon prints, so-called commercially, were distinguished from ordinary direct prints by the appearance of exceedingly delicate tendril, fern, and lace-like motifs, in white or pale colours, on a solid blotch ground. These motifs, which invariably formed part of a 6- or 8-colour floral pattern consisting generally of detached bouquets, were far too delicate in line and dot to be produced by the usual methods of engraving employed for similar effects on a larger scale; that is to say, they could not be "saved for," or reserved, on the blotch roller. Had that been attempted, they would have been obliterated in printing. They were, in fact, engraved on a separate roller and printed in citric acid or citrate of soda or ammonia, over which the blotch colour fell in a solid mass. On steaming to fix the colours, the citrate resists prevented the development and fixation of the superposed blotch colour, with the result that, on washing and soaping, it was removed entirely from the fibre, leaving a clean-cut impression of the under-printed roller. The blotch colours employed for this purpose consisted, in the main, of Alizarins, Persian berries, and Quercitron bark yellows, and mixtures of these with various vegetable dyestuffs and a few of the earlier Chrome colours, the mordants being acetates of aluminium and chromium. Aniline black and Azoic and Basic colours were also available, as blotches, for printing over appropriate resist pastes. The style was attractive in a quiet way and enjoyed a considerable vogue at a time when striking effect and startling design were less popular than at present.

In the process under review, advantage is taken of the same principle, viz. that no fixation of chromium mordants, nor of certain Chrome colours associated with them in printing and padding mixtures, takes place on the cotton fibre in the presence of alkali citrates. On the other hand, these citrates have no effect on the development of Rapidogen and Indigosol dyestuffs; consequently, these colouring matters provide a means for the production of bright and fast coloured resists under Chrome colour grounds.

The process is simple and reliable in application, yields brilliant and very fast coloured resist effects, eliminates the use of sulphoxylates, and permits of the resist colours being printed on white cloth before the ground colour is applied by padding—an advantage of no little practical value, since the slighter defects incidental to printing, such as fine streaks and scumming or smearing, are more or less removed during the subsequent padding operation.

The Chrome colour grounds, too, are of very good fastness, are more economical than grounds of equal depth obtained from other types of resistible dyestuffs of comparable quality, and moreover yield with facility a variety of tertiary shades that are not readily matched with the faster Indigosols and Azoic colours, nor with Basic colours, as used in the much looser Vat-tannic discharge style. The only disadvantage connected with padded Chrome colour grounds—a disadvantage common to all padding styles—is that the drying cylinders require a thorough wash down for every change of colour.

Process.—Print white unprepared cloth with the following Rapidogen and Indigosol resist colours:—

RAPIDOGEN RESISTS.

	1.	2.	3.	4.	5.	6.	7.
	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
Rapidogen Orange G.	80	..	..	..	..	..	..
,, Scarlet R.	..	80	..	..	..	..	..
,, Red R.	..	..	80	..	..	..	..
,, Yellow G.	..	..	..	80	..	..	..
,, Brown B.	..	..	..	..	60	..	..
,, Violet B.	..	..	..	..	..	40	..
,, Blue B.	..	..	..	..	..	..	30
Lukewarm water	130	130	130	130	100	170	130
{Caustic soda 72° Tw.	30	30	30	30	30	30	30
{Methylated spirit	30	30	30	30	30	30	30
Neutral starch-tragacanth paste	500	500	500	500	500	500	500
Glyecine A.	20	20	20	20	20	20	20
Urea	..	..	..	..	50	..	50
Sodium citrate	110	110	110	110	110	110	110
China clay	100	100	100	100	100	100	100
	1000 parts each.						

INDIGOSOL RESISTS.

	1.	2.	3.	4.	5.	6.
	Parts.	Parts.	Parts.	Parts.	Parts.	Parts.
Indigosol Brilliant Pink I. 3 B.	50	..	..	..	..	..
,, Scarlet I.B.	..	80	..	..	..	..
,, Printing Purple I.R.	..	..	60	..	..	..
,, Printing Violet I.B.B.F.	..	..	..	60	..	..
,, O. 4 B.	..	..	..	..	50	..
,, Printing Blue I.G.G.	..	..	..	..	..	60
Fibrit D.	50	50	50	50	50	50
Hot water	80	50	70	70	80	70
Neutral starch-tragacanth paste	500	500	500	500	500	500
Heat up to dissolve—						
Sodium chlorate crystals	100	100	100	100	100	100
Stir in and dissolve—						
Ammonium citrate solution 25° Tw.	150	150	150	150	150	150
Let cool down and add—						
Potassium ferricyanide 1 : 4	50	50	50	50	50	50
Vanadate 1 per cent.	20	20	20	20	20	20
	1000 parts each.					

Print also a white resist paste containing calcium sulphite and zinc oxide or China clay, each of which enhances the purity of the resultant white.

WHITE RESIST.

150	grms.	sodium citrate, crys.
100	,,	calcium sulphite, crys.
500	,,	starch-tragacanth paste.
{125	,,	China clay.
{125	,,	water.
1000		

After printing, the goods are dried and padded, straight through the nip in the usual manner, with, for example, one of the Chrome colour padding liquors given below :—

TYPICAL PADDING LIQUORS.

	1.	2.	3.
Polytrop Blue R.	30 grms.	..	..
Chrome Fast Phosphine R.	..	30 grms.	..
Chromocitronine R.	..	..	20 grms.
Urea	70 ,,	70 ,,	70 ,,
Hot water	500 ,,	500 ,,	500 ,,
Tragacanth thickening	50 ,,	50 ,,	50 ,,
Glyecine A.	20 ,,	20 ,,	20 ,,
Cold water	180 ,,	180 ,,	230 ,,
Chromium acetate 32° Tw.	120 ,,	120 ,,	80 ,,
Acetic acid 50 per cent.	30 ,,	30 ,,	30 ,,
		1000 grms.	

On leaving the padding mangle the goods pass directly over a cylinder drying machine, arranged as near as possible to the mangle, and are dried quickly in order to avoid the formation of halos, then being steamed for 8 minutes in the rapid ager and finished off by washing and soaping at 160° F.

Owing to the addition of acetic acid to the padding liquor the development of the ground and resist colours takes place simultaneously during steaming, and no further fixation treatment is required. If, however, it be preferred to omit the acetic acid from the padding liquor, it will be necessary, after steaming, to develop the Rapidogen colours in the usual way by a few seconds' passage through a hot acid bath of—

30	c.c.	acetic acid 12° Tw.	per litre
10	,,	formic acid 90 per cent.	
30	grms.	sodium sulphate	

at 190°–195° F., followed by washing and soaping.

Almost any Chrome colour which in an unfixed state, after steaming, can readily be washed out of the cloth without leaving a permanent stain, is suitable for use in the foregoing process. Colours fulfilling this condition may be selected from the ranges of almost any important dyestuff manufacturer.

(6) RAISED STYLES.

The term *raised* is an old expression used to signify the method whereby an insoluble metallic salt or oxide or an insoluble colour lake is produced and

fixed on the fibre at one and the same time by a process of precipitation. The most typical example of a raised colour is Chrome yellow, which is obtained by printing or padding the cloth with a soluble (or insoluble) lead salt, and then, after drying, precipitating the lead as lead chromate, by a run through bichromate of soda. Other mineral raised colours are Iron buff, Manganese bronze, and Chrome green. Included also in the raised colour category are the lakes produced by passing goods printed with Catechu solutions and the extracts of Quercitron bark, Persian berry, Logwood, and other vegetable dyestuffs, through hot solutions of bichromate of soda, or of this and ferrous sulphate. Prussian blue is also regarded as a raised colour, since, when printed, it requires oxidising in bichrome, and when dyed it is produced by the double decomposition of Iron buff and ferrocyanide of potash.

Any colours which are raised by the same raising liquor may be printed in combination. Thus Manganese bronze, Iron buff, and sometimes Chrome green may be printed side by side; and similarly, Chrome yellow, steam Prussian blue, and Catechu, Logwood, Persian berry, and some of the red wood extracts, may all be printed together in multicolour patterns.

(*a*) Chrome Yellow and Orange.

These colours are merely the normal chromate (yellow) and basic chromate (orange) of lead. They are both precipitated on the fibre, from a lead salt previously applied, by bichromate of soda or potash, and the orange is obtained by treating the yellow in a bath of boiling lime water which converts it into the basic chromate. The deepest oranges are produced from basic lead acetate.

The thickened solutions may be printed either on plain white cloth or on cloth padded in a 2½–3 per cent. solution of sulphate of soda. Aniline black and any other colour fixed by a short steaming, and unaffected (or developed) by bichromate, may be used in combination with lead yellows.

Yellow P.B.

120 grms.	lead acetate	Dissolve together, and without cooling add—
100 ,,	lead nitrate	
450 ,,	water	
80 ,,	flour	previously mixed into a paste.
250 ,,	water	
1000	Boil and cool.	

Yellow P.B.C.

650 grms. lead carbonate 50 per cent. paste.
250 ,, British gum paste 25 per cent.
100 ,, starch paste 12½ per cent.

1000

This yellow is suitable for working with Aniline black.

Lead Carbonate (for above).

34 kilos. lead acetate.
100 ,, water.

Add gradually, whilst constantly stirring—

12 kilos. soda-ash.
100 ,, water.

Allow the precipitate to settle, and wash 3 times by decantation; then filter until the paste contains 50 per cent. of lead carbonate. The above quantities = 47·9 kilos. of 50 per cent. paste.

ORANGE P.B.

200 grms. lead acetate.
100 ,, lead nitrate.
560 ,, water.
90 ,, British gum paste.
50 ,, flour or starch.

1000 Boil and cool.

ORANGE P.B.B.

{50 litres basic lead acetate solution.
{ 5 kilos. flour.

Boil and cool.

BASIC LEAD ACETATE SOLUTION.

900 grms. water.
600 ,, lead acetate.
225 ,, litharge.

Boil one hour, allow to settle, and use the clear supernatant liquor for Orange P.B.B.

All the above colours are printed, dried, and developed at once in various Chrome baths according to the shade desired.

CHROME BATHS.

For—	YELLOW P.B.	YELLOW P.B.C.	ORANGE P.B. or P.B.B.
	grms.	grms.	grms.
Bichromate of soda . .	25	25	100
Sulphate of soda . .	100	..	..
Common salt . . .	..	100	200
Water	1000	1000	1000

The printed goods are chromed at the full open width and in a continuous manner at 80°–85° C.; the rate at which they pass through the chroming beck depends upon its size, but should be adjusted so that the cloth is given about two minutes' immersion in the liquor. After chroming, the goods are well washed and, if required, open-soaped before drying.

For oranges, the pieces after chroming are washed and passed through a clear boiling lime-water bath containing 40 grms. of quicklime and 10 grms. bichromate of soda per litre of water. Wash well and dry.

Patterns containing Aniline black and the extracts of Logwood, Bark, etc., or steam Prussian blue, must be steamed in the rapid ager before chroming.

(b) Iron Buff.

Iron buff (oxide of iron) is produced by printing ferrous acetate or ferrous sulphate, followed by a run through caustic soda and subsequent exposure to the air.

Iron Buff Printing Colour.

500 grms.	ferrous acetate. (See Mordants.)
500 ,,	British gum paste.
1000	

Print, dry, and pass the goods through caustic soda 4° Tw. at 75° C.; allow to lie in pile until the ferrous hydrate is fully oxidised, and then wash off in water.

The process is expedited by a short steaming through the rapid ager before raising in caustic soda, or the pieces may be treated in a dilute solution of bleaching powder after the caustic bath, or, again, the bleaching powder may be added to the caustic soda.

Iron buff in combination with Aniline black is largely used as a blotch in the production of black and buff handkerchiefs for the East. It is very fast to soap and alkalies, but sensitive to the action of acids.

(*c*) Manganese Bronze.

The dyeing of Manganese bronze for discharging has already been described in detail. The production of printed patterns is practically identical, the only difference being that Manganese chloride is printed instead of being padded on the cloth. In other respects the process is the same.

Manganese Bronze Printing Colour.

850 grms.	manganese chloride 70° Tw.
150 ,,	British gum.
1000	

Print, dry, pass through caustic soda, wash, pass through bleaching powder solution, wash, and dry. For full details of these operations, see Bronze Discharge Styles.

(*d*) Chrome Green.

This colour is seldom used as a self shade. It may be produced by any of the many methods of mordanting cotton with chromium oxide. The cloth may, for example, be printed or padded in a strong solution of a basic chromium sulphate (say chrome alum made basic with soda-ash), dried, steamed 2–3 minutes in the rapid ager, and then passed at once through a hot solution of soda-ash, which precipitates the chromium hydroxide, or Chrome green.

The well-known Khaki shade is a mixture of Iron buff and Chrome green, and is obtained by precisely the same means, from a solution containing chromium and ferrous acetates or other salts of iron and chromium.

(*e*) Prussian Blue.

The production of Prussian blue has been described at length elsewhere in this volume. (See Discharge and Steam Styles.) Steam Prussian blue always requires a run through a bichromate bath to bring about the full development of its shade, and for this reason it is mentioned here, although, properly speaking, it is not a raised colour in the general sense of the term. On the other hand, Prussian blue dyed by treating Iron buff dyed cloth in an acid solution of yellow prussiate is a true raised colour, since both the buff and the blue are precipitated directly upon the fibre.

(*f*) Raised Vegetable Colours.

A modification of the well-known wool-dyeing method of "stuffing and saddening" may be applied, in certain cases and for particular styles, to the fixation of some vegetable dyestuffs on cotton cloth. Of these, Catechu is the most important; but others, such as Persian berries, Quercitron bark, and Logwood, are also useful, inasmuch as they permit of compound shades being obtained and multicolour effects produced without any variation of process. The multicolour effects obtained are limited to combinations of brown, yellow, olive, drab, fawn, grey, and such mode colours as can be mixed from Catechu, Logwood, and the yellow dyestuffs.

Much variety, however, can be introduced by the printing of steam Prussian blue, Aniline black, and (or) the Logwood iron black J. (already described in the sections on the Steam and Azoic colour Styles, see p. 518), along with the colouring matters mentioned above.

The process consists in printing thickened solutions of Catechu and other natural dyestuffs on white cloth, and then, after drying, passing the printed goods through a hot bath of bichromate of soda, which reacts with the dyestuff to form an insoluble colour lake. A slight addition of alkali to the printing colour improves both the shade and the intensity of the ultimate result, and a run through the rapid ager before chroming has a beneficial influence upon the fastness and evenness of the colours. If Prussian blue, either as a steam colour or in the form of a solution in oxalic acid, is used in conjunction with Bark, Persian berries, or Logwood extracts, for olives, greens, and slates, the alkali must be omitted from the printing pastes, otherwise the blue will not develop.

Bright greens, yellows, and blues are obtained from lead salts, Prussian blue, and mixtures of the two, and blacks from Aniline black, Diphenyl black, and Black J. (p. 518). Logwood alone raised in chrome does not give a good black; it is only suitable for greys and compound shades. Alizarin blue S. with zinc or chromium mordants yields a fine bluish shade of slate, and may be added to the vegetable dyestuffs.

All patterns containing steam colours, in addition to the raised or developed colours, must be steamed in the rapid ager for 3–4 minutes previous to chroming; and only such steam colours as are fixed by a short steaming should be employed, as prolonged steaming causes the raised colours to run.

The following recipes are taken from practice:—

GREY R.L.

160	grms.	Logwood extract 32° Tw.
20	,,	glycerine.
800	,,	tragacanth thickening 4 per cent.
20	,,	caustic soda 70° Tw.
1000		

BROWN R.C.

240	grms.	Catechu (in cubes).
320	,,	water.

Dissolve and strain into—

480 grms. tragacanth thickening 6 per cent.

Boil, cool, and add—

80 grms. caustic soda 35° Tw.

And, before printing—

5	grms.	copper sulphate 10 per cent. solution.
5	,,	magnesium acetate 32° Tw.
1130		Boils down to about 1000 grms.

YELLOW R.B.

760	grms.	tragacanth thickening 4 per cent.
100	,,	Persian berries extract 52° Tw.
100	,,	Bark extract 52° Tw.
20	,,	glycerine.

Boil, cool, and add—

20 grms. caustic soda 70° Tw.

1000

OLIVE :—	4 to 8 Yellow R.B. 1 to 1 Grey R.L.
FAWN :—	6 Brown R.C. 6 Yellow R.B. 1 Grey R.L.
GREEN :—	2 to 6 Yellow R.B. (without caustic soda). 1 to 1 Prussian blue sol. 30 per cent. (in oxalic acid).
BRIGHT GREEN :—	4 to 48 Yellow P.B. (see raised yellows). 1 to 1 Prussian blue sol. 30 per cent.

YELLOW :—Yellow P.B. or P.B.C. (raised yellow).

BLACK :— Aniline, Diphenyl, or Logwood iron blacks.

BLUE :— Steam Prussian blue.

SLATE :— Alizarin blue S., with zinc sulphate.

Print all the foregoing colours on white unprepared cloth ; dry and steam 3–5 minutes in the rapid ager ; pass continuously through a 1–2 per cent. solution of sodium bichromate at 80°–85° C., wash well, and dry. Somewhat better results are secured by hanging the steamed goods in a warm chamber before chroming. In the case of Catechu, a darker shade is obtained after 2–3 days' exposure to warm air.

The above described style is almost obsolete, though it is still used occasionally on the Continent for certain classes of heavy dull-coloured furniture cretonnes.

(7) PRINTING OF LININGS (PASTE COLOURS).

Most of the linings used by clothiers and dressmakers are printed with striped patterns, and where the whole surface of the material displays the same texture they are produced by means of the ordinary steam colours.

Some classes of linings, however, have the appearance of brocade stripes—that is, one stripe is lustrous while the next has a dull matt surface. This latter effect is obtained by printing zinc oxide either alone or tinted with Pigment, Direct, or Basic colours. The zinc oxide is fixed with albumen, and it retains its dull, pasty appearance even after the cloth has been heavily calendered, or Schreinered, to give a lustre to the unprinted portions. Naturally, the best contrast is obtained by printing zinc white on sateen cloth, and especially on mercerised sateen that is subsequently "lustred" in the Schreiner calender. Other patterns may, of course, be employed at will in place of stripes, and many beautiful brocade or damask effects are obtained by printing various patterns in zinc oxide colours on white or tinted grounds.

ZINC OXIDE PRINTING PASTE.

350	grms.	zinc oxide.
50	,,	glycerine.
250	,,	egg albumen 50 per cent. solution.
250	,,	6 per cent. tragacanth thickening.
70	,,	olive oil.
30	,,	turpentine.
1000		

Grind the whole until it will pass easily through a straining cloth.

Print, steam in the rapid ager, and then finish without any further treatment. The above colour gives fine white damask effects on both white and tinted grounds.

For coloured effects of the same sort, an addition of any suitable colouring matter is made to the white paste. For this purpose any Basic, Direct, or Pigment colour may be used, the quantity taken depending on the shade required. Generally, very light shades give the best results.

The majority of linings are printed on white or delicately tinted grounds, and when a dark colour enters into the pattern it is usually one of the ordinary steam colours. The grounds are tinted with direct dyeing colours in the padding machine. Black, red, claret, brown, blue, and other dark ground linings are produced by any of the discharge or reserve processes already described—*e.g.* Aniline black, Paranitraniline red, Paramine brown, Naphthylamine claret, Diaminogene blue, Sulphur colours, etc.

Besides zinc oxide, barium tungstate, barium sulphate, lead sulphate, and Lithopone are also used for damask effects. Tungstate of barium yields an exceedingly brilliant white, while the sulphates of lead and barium are only used for inferior and cheaper work. They (the two latter) are by-products from the preparation of aluminium acetate and sulphocyanide.

(8) METAL PRINTING.

The production of permanent metallic effects on textile fabrics is a problem which has occupied the attention of calico printers for a very long time.

Apart from the technical difficulties encountered in the printing of pastes containing a high percentage of metal in the form of a finely divided powder, it was impossible, formerly, to obtain solid-looking prints which were fast to washing and were unaffected by the action of impure air. At first sight it would appear that metallic powders could be treated like pigment colours, and fixed like, say, Chrome yellow which is fixed with albumen. Such a process, however, does not yield satisfactory results: the prints are uneven, poor in colour and lustre, and lack the body and solidity so characteristic of the gold and silver woven and embroidered effects which first suggested the idea of applying metallic powders by printing. The heavy metallic powders settled in the colour box and stuck in the engraving, and the chemical action of albumen, which contains sulphur, blackened the "gold" and "silver" powders, owing to the formation of copper and tin sulphides. The substitution of oil varnishes gave much more satisfactory results so far as regards brilliancy and permanency, but the method of printing mixtures of "gold" and "silver" and varnish with ordinary engraving left much to be desired in the way of solidity of appearance; in fact, the method was little used on this account. The most successful of the old processes of metal printing consisted in applying a sticky paste of glue and starch to the fabric, which was then passed directly, before the paste was dry, through a closed box, in which bronze powder was lightly

brushed on the cloth. On leaving the bronzing box, the cloth passed continuously through a series of closed boxes fitted with guide rollers and beaters, which latter, acting on the under side of the cloth, beat off all the gold powder not adhering to the printed parts. The goods were then hung in a dry, warm room in order to harden the glue vehicle, and, after a thorough brushing to remove all loosely adhering powder, were calendered to burnish the metal. In this way very effective and solid-looking metallic patterns were obtained, but unfortunately they were neither fast to washing nor to the blackening influence of impure air. Goods printed by this process were intended mainly for decorative hangings in theatres and the like, and consequently their liability to blacken in a gas-laden atmosphere was a serious drawback. With improved methods, however, many of the defects of earlier processes have been overcome; so much so, indeed, that even fine patterns are now printed on dress goods—patterns which retain their metallic lustre after washing and a long exposure to all sorts of air.

These improvements date from the introduction of the continuous stencilling machine patented by S. H. Sharp in 1894. Sharp's machine provided the first practicable means of producing fast, solid, metallic prints.

The metallic powder mixed with varnish was stencilled on the cloth, and the varnish was then dried by hanging the goods for several days in a warm, dry atmosphere; when quite dry and hard, the lustre of the metal was brought out by calendering. Prints executed in this way are remarkably permanent, and stand a severe soaping if the temperature is not too high; in the cold they are practically unaffected by strong caustic soda, a property which allows of them being "crimped," according to the methods to be described when dealing with the Crimp or Crepon style.

As Sharp's apparatus was patented, other methods were sought of producing similar results by means of the ordinary cylinder printing machine.

Previous attempts to print metallic varnishes with engraved rollers had given unsatisfactory work, but the problem was attacked afresh, and finally it was discovered that the cause of the earlier failures was due entirely to unsuitable engraving. The ordinary engraving of masses consists of a series of corrugations or furrows (the ground), which, although essential to the printing of starch, flour, gum, and albumen colours, are altogether inadequate to the production of first-rate metallic prints. The metal is not only apt to stick in and fill up the engraving, but even when a brush furnisher is used to keep the furrows clear of deposit, the amount of colour transferred to the cloth is insufficient to give a solid effect on calendering. The engraving adopted for metal printing is deep and smooth, without any furrows or other roughness whatsoever. Usually the pattern is etched out with nitric acid, and many worn-out copper rollers, useless for ordinary printing, can be utilised for metal printing by re-etching them deeply, so as to dissolve away most of what ground may still remain. From such deep, smooth engraving a heavy charge of colour is transferred to the cloth, and, with a brush furnisher, no difficulty is experienced in printing varnish mixtures containing as much as 25–30 per cent. of gold or silver powders.

A good quality of hard-drying copal varnish is the best medium to use for the printing and fixing of the various bronzes and silvers. The metallic powders or bronzes consist of finely divided alloys of copper and tin, with sometimes zinc and lead; silver is either tin or aluminium, generally the latter. Gold bronzes vary in shade from the deep red of copper to the palest tint of gold; and, besides these and the silver, there is a variety of crimson, blue, green, orange, olive, and other shades of so-called bronzes. Sometimes these coloured bronzes are mixed with aluminium powder to enhance their lustre.

The printing of bronze powders is carried out in the usual manner, but the goods are not passed through the drying apparatus; in fact, it is quite impossible to run them under and over a series of rollers, because the varnish, being sticky, would soil anything with which it came in contact. Instead of the ordinary drying, therefore, the printed cloth is drawn right over the drying machine and plaited down between greys, the printed side to the grey cloth. Some little bronze sticks to the grey, but the loss is too slight to affect the ultimate result to any appreciable extent. It is an advantage to employ damp greys, since the presence of moisture prevents the varnish attaching itself to the grey. From the printing machine, the goods are taken to a hot, dry hanging room, and there suspended until the colour is dry and hard; then, without further treatment, they are cold calendered and made up.

Gold Bronze.

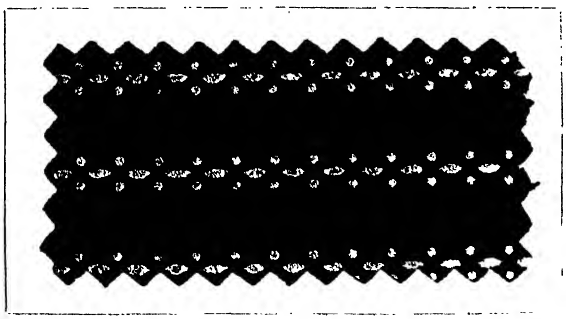
250	grms.	Bronze powder.
750	,,	copal varnish.
1000		

" Silver."

100–150	grms.	aluminium powder.
900–850	,,	copal varnish.
1000 1000		

Other bronzes are prepared for printing similarly. Print; plait down between greys; hang 3–6 days in a dry, warm ageing chamber; calender and finish.

Metal printing with varnish is confined to a few styles. It is not suitable for white or delicately tinted cloth, as the oil in the varnish spreads by capillary attraction beyond the edges of the pattern. On light grounds this causes an unsightly yellow stain all round the printed objects, whereas on dark grounds it is unnoticeable, though present. Moreover, dark blue, green, black, claret, purple, etc., contrast much better with gold and silver than pale pinks and the like. Again, very few colours are available for printing alongside bronzes, because the lustre of the latter is impoverished by the acid fumes generated in the steamer. On blue grounds a Logwood iron black and green zinc oxide colour (see Linings) may be printed with good effects alongside a gold bronze, but as they cannot be steamed they are not fast, and are only suitable for temporary decorations, which are not expected to stand washing.



Metal Print (C.P.A.).

On goods already dyed, steamed, and finished, a cover pattern is often printed in bronzes. In such cases a combination of steam prints with metallic

effects is obtained, but the two patterns do not register with each other, and the steam or dyed colours can scarcely be said to have been worked in combination with the bronze cover print. Most of the metallic prints produced to-day are small spots, sprigs, and stripes on sateen cloth, previously dyed in various dark shades. They had a great run some years ago, but never became, nor are likely ever to become, fashionable.

An excellent method of printing metallic powders, without recourse to special engraving or other arrangements, and free from the above-mentioned disadvantages, was introduced into practice at the works of J. Heilmann & Co. by Hugo Wagner and Martin Battegay.[1]

Taking into consideration the fact that ordinary combined fixing and thickening agents, such as albumen, casein, and glue, do not give, when coagulated, sufficiently fast prints; and also the difficulties connected with the employment of varnishes both in printing and drying, the inventors sought to find an entirely new fixing agent which should be free from these drawbacks. Such a fixing agent must, in the first instance, possess sufficient viscosity to maintain the metallic powder in suspension in order to prevent it from filling up, or sticking in, the engraving during printing. Attention also was directed to the influence of the solvents usually employed. Many of these are impracticable on account of their volatility, and others, both acid and alkaline, which in general are only slightly harmful, exercise a very detrimental effect when applied to metal printing. Thus, although the acetyl-celluloses furnish satisfactory thickeners, their solution in acetic acid is unsuitable for the purpose, since the comparatively feeble acid has an energetic action on finely divided alloys of copper, tin, and aluminium.

A systematic study of the solubility of acetyl-cellulose (Sericose) finally led to the adoption of a mixture of phenol and formaldehyde as solvent. The solution of acetyl-cellulose, obtained in this way, had no action on the metallic powders and gave a good printing compound, but it did not prevent the metallic powders from sticking in. This defect was, however, overcome by taking advantage of the possibility of forming the condensation products of phenol and formaldehyde.

These two bodies react, especially in presence of small quantities of acetate of soda, acetate of ammonia, etc., to form the well-known synthetic resin, Bakelite. On heating the above solution of Sericose in phenol and formaldehyde on a water bath, the two latter bodies condense to form one of the many viscous intermediate products obtained during the condensation of phenol and formaldehyde. The resulting thickening is mixed with about 25 per cent. of bronze (gold) powder, and printed either alone or in combination with other colours, on white or dyed cloth. On steaming (and partly also during drying) an insoluble synthetic resin is produced, which, in conjunction with the acetyl-cellulose (Sericose), fixes the gold powder on the fibre in such a way that it becomes fast to soaping.

During the steaming all excess of phenol and formaldehyde is driven off, leaving the fabric inodorous.

The printing colour is prepared as follows:—

THICKENING:—	150	grms.	Sericose.
	450	,,	phenol (or other similar phenol).
	500	,,	formaldehyde 40 per cent.
	50	,,	dry acetate of soda.
	1150		

[1] *Bull. de la Soc. Industrielle de Mulhouse*, 1913, p. 234.

Heat several hours in a jacketed pan, or on a water bath, after the Sericose is dissolved, and then add the necessary amount of any desired metallic powder, for example :—

Printing Colours.	Gold.	Silver.
Gold bronze powder	250 grms.	..
Aluminium ,,	..	150 grms.
Above thickening	750 ,,	850 ,,
	1000	1000

Print, dry, and steam 4–5 minutes in an ager ; wash, soap, and dry ; then calender to burnish the metallic print.

Metal prints obtained by this method are remarkably resistant to acid fumes, so much so in fact that the metallic colour may be worked along with discharge colours on slop-padded Aniline black and also on grounds of the Azoic and Direct colours. In this respect they are infinitely superior to anything hitherto suggested.

A modification of the process consists in employing glue and resorcin in place of phenol and Sericose.[1] The results are satisfactory, but the prints are not so fast as those described above.

Another process, in which acetyl-cellulose alone acts both as fixing and thickening agent, has been successfully worked, on the large scale, by J. Frossard and C. Rebert, at the works of N. N. Konchine, Serpoukoff, near Moscow.[2] The Sericose (acetyl-cellulose) is dissolved in phenol, acetone, and alcohol, and, as "Bakelite" is not in question, the presence of formaldehyde is unnecessary. The absence of formaldehyde is of great practical importance, as its presence in large proportions renders the work of the printers and various assistants most disagreeable and dangerous.

The compositions of the printing pastes are, according to circumstances, as follows :—

1. 125 grms. Sericose (or similar compound).
   350 ,, phenol 90 per cent.
   300 ,, methylated spirit.
   250 ,, commercial acetone.

Or

2. 125 grms. Sericose.
   350 ,, phenol 90 per cent.
   525 ,, commercial acetone.

The bronze powders are added in suitable proportions.

The Sericose dissolves easily in the cold ; more rapidly if heated on a water bath.

The greater part of the solvents is driven off during the passage of the printed goods through the drying chambers connected with the printing machines, and partial fixation of the metallic powders takes place at this stage. But a certain amount of phenol is still retained by the cloth, and can only be removed by a short steaming in a rapid ager—an operation which completes the precipitation of insoluble Sericose, and finally fixes the bronze and, at the same time, frees the goods from the odour of phenol.

Colours made as above are distinguished by their great fastness. Boiling soap is without action on them ; and if they are printed along with ordinary steam colours, or with discharges on dyed grounds, they withstand all the

[1] J. Stephan: *Bull. de la Soc. Industrielle de Mulhouse*, Jan. 1913.
[2] *Ibid.*, 1913, p. 648.

after-treatments demanded by these styles (steaming, fixing in tartar emetic, soaping, etc.). They work well in the printing machine, do not stick in the engraving, and keep almost indefinitely provided the solvents are not acid.

(9) CREPON OR "CRIMP" STYLE.

The characteristic feature of this style is the appearance of alternate plain and crinkled stripes in the fabric itself. Sometimes one, sometimes the other, and sometimes both of these two sorts of stripes are coloured; at other times they simply take the colour of the pattern over which they run.

The crinkled stripes, known as "crepon" and "crimp" stripes, are produced by a process based upon the property possessed by concentrated solutions of caustic soda, of causing cotton to shrink. Cotton cloth, printed in a stripe pattern with strong caustic soda, shrinks in the printed parts, and thus causes the unprinted parts to cockle or crumple up. The greater the shrinkage or contraction of the printed parts, the more pronounced is the crepon effect obtained.

Coloured stripes are produced by the addition of direct-dyeing dyestuffs either to the caustic soda or the paste used for printing the stripes to be crimped or creponed.

Similarly, Direct dyestuffs are employed for printing the patterns on cloth that is subsequently covered or otherwise treated in strong soda lye. But for this latter purpose any colours that are unaffected by caustic soda solutions —*e.g.* Aniline black, Indigo, and other Vat dyestuffs, Sulphur colours, Paranitraniline red, Naphthylamine claret, many Chrome colours, and even Victoria blue (basic colour)—may be employed, either alone or alongside the Direct dyestuffs, so that the crepon style is capable of being applied to a great variety of purposes. In addition to the direct printing of multicolour patterns on white grounds, discharge and resist effects are easily obtainable on Aniline black, Paramine brown, and Vat, Azoic, and Direct colour grounds.

There are two methods of producing crepons:—

(*a*) By the direct printing of caustic soda.

(*b*) By printing the parts of the cloth to be crimped with a gum resist, and afterwards padding the goods through caustic soda in a small padding machine.

By the first method it is impossible to print a design between the crepon stripes; that is, the plain stripe must always be white or a flat tint. By the second method any kind of pattern may be applied to the plain stripe, since the caustic soda treatment is a separate operation, and the goods can therefore be steamed or undergo any other suitable process before they are padded in caustic soda. In neither process of crimping is it usual to decorate the crimp stripes, not because it cannot be done easily enough by engraving for the purpose, but because the effect is bad. In some cases, however, the crepon or crimp stripe consists of several colours, arranged somewhat after the fashion of a continuous upright spectrum.

(*a*) **Direct Process of Crimping.**

In this process the cloth is printed with a thickened solution of caustic soda corresponding to between 50°–90° Tw. A pattern of any number of stripes may be employed, and by suitably distributing the caustic colours and the ordinary colours between the several rollers, either the plain or the crimp stripes, or both, may be produced in a variety of shades. Dark reds, clarets, and blues are obtained by printing Azoic colours on naphthol-prepared cloth, along

with caustic soda colours in the other rollers; such reds, clarets, and blues necessarily appear in crimped stripes only, since the addition of caustic soda to Azoic colours would prevent their coupling with the naphthol. Aniline and other blacks, and dark colours generally, are unobtainable (in fitted stripes) by the direct method of crimping, on account of the fact that the goods cannot be steamed with any degree of satisfaction. Apart from that, too, the scumming of the caustic soda influences them unfavourably. Some of the Vat dyestuffs might possibly be applied successfully, as the marking off of the caustic soda on the rollers of the ager would not be likely to affect them prejudicially.

I. Caustic Soda Printing Colour 64° Tw. (for Plain White Stripes).

6·400 litres caustic soda 100° Tw.
3·600 ,, gum Senegal 35 per cent. solution.

10 litres

Add the soda to the gum gradually, stirring all the time.

II. Caustic Soda Printing Colour (for Plain Coloured Stripes).

6·4 litres caustic soda 100° Tw.

Add gradually to—

3 litres gum Senegal 40 per cent. 250 grms. Direct dyestuff. 350 ,, water (boiling).	Mix the dyestuff with the water; then add the gum, and heat until the dyestuff is dissolved.

To 10 litres

For Pink take:—Brilliant geranine B.
,, Yellow ,, Diamine fast yellow A.
,, Blue ,, Diamine sky blue F.F.
,, Green ,, 2 parts blue; 7 parts yellow.
,, Violet ,, 2 parts pink; 1 part blue.
,, light shades, any of the above, reduced with caustic soda gum 64° Tw. as above.

If the crimp stripes are to appear in colours other than Azoic colours, the Direct dyestuffs are again employed, but made up in the following manner:—

Colours for Crimp or Crepon Stripes.

25 grms. Direct dyestuff.
400 ,, water.
30 ,, phosphate of soda.

Dissolve, and stir into—

545 grms. 6 per cent. tragacanth thickening or starch paste.

1000

Heat the whole until the dyestuff is perfectly dissolved, and then cool down.

According to this recipe, almost all Direct dyestuffs may be employed. Light shades are obtained by adding extra thickening as required.

In order to obtain the best results as regards the prominence of the crepon stripes, the caustic colours should occupy at least half the surface of the cloth; indeed, the very best crepon effects are secured by printing the caustic colour in broad stripes, leaving only narrow stripes of unprinted cloth, or cloth printed in

colours containing no caustic soda, between each broad stripe. In this way the greater part of the cloth undergoes considerable shrinkage, thus causing the lesser part, which is not subjected to the action of the caustic soda, to crimp in the most pronounced fashion.

One example of the method of producing a four-colour pattern by the Direct Method of Crimping will illustrate sufficiently the principle of the general *modus operandi*. For instance, to obtain an effect consisting of red, blue, and yellow crimp stripes, with broad white plain stripes between them, the cloth is first of all prepared in β-naphthol as usual.

It is then dried and printed for the colours in Paranitraniline red, Diamine sky blue F.F., and Diamine fast yellow A., all thickened with tragacanth, starch or British gum, and for the White, with caustic soda 64° Tw., thickened with either gum Senegal or tragacanth. After printing, the goods are run through the air for a short time with as little tension as possible, to allow the mercerised cloth to contract to the fullest extent; they are then passed through a hot-air chamber and partly dried to prevent marking off, and finally they are washed thoroughly in cold running water, soured in dilute sulphuric acid, washed again, and dried over cylinders or in hot air. In the wet state no more tension than is necessary should be put on the goods, otherwise they are liable to stretch, and so lose a good deal of their crepon effect.

Instead of printing the foregoing colours on white cloth, whereby stripe patterns only are possible, a good deal of variation can be obtained by printing them on cloth already printed in a multicolour floral or other pattern. In this case the previously applied pattern must, of course, be in colours that will withstand the action of caustic soda. Similarly, blotch patterns may be crimped with good effect; in fact, any suitably resistant colour may be utilised in this way to advantage. Amongst the colours that withstand caustic soda the following may be mentioned:—Azoic reds, clarets, oranges, and blues, Victoria blue (tannate of antimony mordant), Silvertown blue dyed on iron mordant, Chromocitronine, Alizarin blue S., Iron buff, Indigo, the Sulphur, Vat, and most of the Direct dyestuffs. Aniline black is also pre-eminently adapted to crimping after development.

(*b*) Resist Method of Crimping.

This process, which is due to John Mercer, is founded on the fact that thick solutions of gum Senegal, gum Arabic, gum Gedda, or British gum, when printed on cotton cloth, form, when dry, efficient resists to the mercerising or shrinking action of caustic soda. They act mechanically by preventing the soda from coming into contact with the fibre during the subsequent crimping operation, which consists in padding the printed goods, through caustic soda, in a padding machine.

On the other hand, gum tragacanth, at the strength used for thickening colours, offers no appreciable obstruction to the absorption of caustic soda by the fabric, and therefore it can be used safely for the production of the plain stripes when these are required in colour, or when a plain white stripe is required to be decorated with a printed design.

By a plain stripe is understood a flat, uncrinkled stripe, irrespective of any pattern it may carry.

The same colours that are used for the Direct Process are used for the Resist Process, but in the latter they are capable of being applied to a much wider range of patterns; in fact any multicolour pattern containing a solid stripe can be executed by the Resist Crimp process as easily as by any other

ordinary method of printing. All that is necessary is to use alkali resisting colours thickened with tragacanth in the plain, smooth stripes, and similar colours thickened with gum Senegal or British gum for the crimp stripe or stripes.

Apart from its wider scope, the Resist Process offers another great advantage over the Direct Process, inasmuch as the printed goods can be steamed before they are treated in caustic soda. This facility is not only of immense value as regards the better fixation of the colours, but it also makes possible the production of many crepon effects otherwise unobtainable. For instance, Aniline black may be employed as a part of a multicolour pattern that registers with the crepon stripe ; or, again, resist effects on an Aniline black ground in combination with a white or coloured crepon stripe may be as easily obtained as by the usual Aniline black resist process. Neither of these styles is possible by the Direct Method of Crimping.

In practice, either gum Senegal or a dark British gum is used for printing the parts of the cloth to be crimped.

British gum is the cheaper, and for any but the most delicate shades quite as effective a resist as gum Senegal.

Gum tragacanth is employed solely for printing the uncrimped parts of the cloth, and for this purpose it has no competitor.

For convenience of description, colours thickened with dark British gum will be distinguished as "B.G. colours," while those thickened with tragacanth will be referred to hereafter as "G.T. colours." It may be well to note that "B.G. colours" may sometimes contain gum Senegal for the purpose of improving their working qualities: this, however, does not demand any modification of nomenclature, since both gums play the same rôle.

The separate operations connected with the Resist Crimp Process are as follows:—

(1) Print the cloth with the required B.G. and G.T. colours.

(2) Dry and steam 3–60 minutes according to circumstances.

(3) Pad straight through the nip in caustic soda 50°–60° Tw. Allow to lie a short time, and then—

(4) Wash well in the rope form until the goods are free from soda.

(5) Sour in sulphuric acid $\frac{1}{4}$° Tw., wash, and dry.

If the patterns contain such colours as Benzopurpurine or Congo red, it will be necessary to treat them in dilute ammonia after the last wash out of sours in order to re-develop their bright red colour, which is turned blue by acid.

In the case of Aniline black resists, the printed goods are best steamed for 45–60 minutes after printing; they are then padded in Aniline black P. or P.S. (see Black Discharges, p. 773) in the usual manner, dried and steamed 3–4 minutes in the rapid ager at 90°–94° C. The rest of the process is as above.

The following formulæ have given excellent results on the large scale:—

Resist B.G. (for White Crimp Stripes).

500	grms. dark British gum.
500	,, water.
1000	

Boil and cool. Best used slightly warm.

B.G. Colours for Crimp Stripes.

	Red B.G.	Pink B.G.	Yellow B.G.	Blue B.G.	Green B.G.
Congo red	50	..	..	..	..
Brilliant geranine B.	..	25	..	..	..
Diamine fast yellow A.	..	..	25	..	..
Thioflavine S.	..	..	..	..	18
Diamine sky blue F.F.	..	..	..	25	6
Phosphate of soda	50	25	25	25	26
Water	475	500	500	500	500
Dissolve and add—					
Dark British gum	425	450	450	450	450
Heat together until the gum is dissolved, and cool.					
	1000	1000	1000	1000	1000

Other shades are obtained by mixing the above.

G.T. Colours (for Plain Coloured Stripes or for Patterns on Plain White Grounds).

Type:—

25 grms. Direct dyestuff.
25 ,, phosphate of soda.
475 ,, water.
475 ,, 6 per cent. tragacanth thickening.

1000 Boil and cool.

For the various shades use the same dyestuffs as are used for B.G. colours. Instead of Congo red, Paranitraniline red (printed on naphtholated cloth) may be used for heavy plain stripes. When Congo red is employed, the addition of albumen is beneficial in preventing it from running.

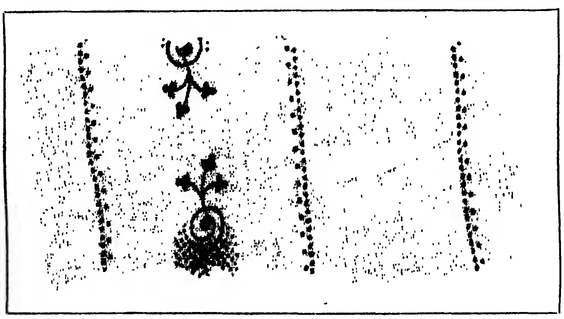
Examples:—

(1) *Pink crimp stripes with Three-colour pattern between them.*—Print the stripes with Pink B.G. and the pattern between with Blue G.T., Green G.T., Yellow G.T. Dry.

(2) *Pink crimp stripe and Green plain stripe.*—Pink B.G. and Green G.T.

(3) *White crimp stripe and Red plain stripe.*—Print Resist B.G. for the white and Paranitraniline red (tragacanth thickening) for red on naphtholated cloth. Dry.

(4) *White crimp stripe on plain Black ground.*—Print Resist B.G. containing 30 per cent. acetate of soda on Aniline black padded cloth. Dry.



Gum resist Crimp (C.P.A.).

Nos. 1 and 2 may be steamed 45 minutes ; No. 3 is not steamed at all ; and No. 4 is steamed 3–4 minutes and then dried. All are then padded in caustic soda 63° Tw., washed well, soured, washed, and dried. In padding, the goods pass directly between the bowls of the padding machine ; the bottom bowl is partly immersed in the caustic liquor, and supplies a sufficiently large charge of caustic soda to the cloth, without the risk of dissolving the resist. Wherever the B.G. colours have been printed the cloth "cockles," and on washing out the resist it assumes the well-known appearance of the crepon effect.

The Aniline Black Resist Style in Crepons.—By combining the zinc oxide process of reserving Aniline black with the resist method of crimping, it is possible to obtain a great variety of coloured crepon effects, in which the plain stripe displays a floral pattern in several colours on a black ground, while the crimp stripe may be in white or colours according to the pattern in hand. The advantage of this method is that the crimp stripe is an integral part of, and fits to or registers with, the floral or other portions of the pattern.

With the exception of an addition of zinc oxide, the colours used are essentially the same as the B.G. and G.T. colours already given. They are prepared according to the following directions:—

(*a*) For Crimp Stripes.

B. Resist White B.G.

200	grms.	precipitated chalk.
50	,,	potassium sulphite 90° Tw.
50	,,	acetate of soda.
375	,,	water.
325	,,	dark British gum.
1000		

Beat the whole into a smooth paste, heat until the gum is dissolved, and cool.

B. Resist White B.G. gives a better white under the black than zinc oxide. Zinc oxide, however, is to be preferred for colours, because it works better in printing and yields brighter shades. It is usually ground up with a little glycerine, and turpentine is added to minimise the tendency to froth.

Z. Paste B.G. (for Colours) Standard.

200	grms.	zinc oxide.
170	,,	water.
25	,,	glycerine.

Beat into a paste, and add—

200	grms.	dark British gum.
150	,,	gum Senegal 50 per cent. solution.
30	,,	turpentine.
775		

Heat to dissolve the gum, and then use warm or cold.

B. Colours B.G. (Crimp Stripes).

	B. Red B.G.	B. Pink B.G.	B. Blue B.G.	B. Gold B.G.	B. Yellow B.G.
Congo red	50	..	..	..	..
Brilliant geranine B.	..	25	..	..	..
Diamine sky blue F.F.	..	..	25	..	..
Diamine fast yellow A.	..	..	..	25	..
Thioflavine S.	..	..	..	..	25
Water.	150	175	175	175	175
Phosphate of soda	50	25	25	25	25
Dissolve and add—					
Z. Paste B.G. Standard	700	775	775	775	775
Albumen 40 per cent.	50	..	..	..	..
	1000	1000	1000	1000	1000

Green = 3 parts Yellow to 1 part Blue.
Violet = 2 ,, Pink ,, 1 ,, Blue.
Olive = 3 ,, Gold ,, 1 ,, Blue.
Orange = 6 ,, Gold ,, 1 ,, Pink.
Salmon = 3 ,, Gold ,, 1 ,, Pink.
Fawn = 14 ,, Pink, 5 parts Gold, 1 part Blue.

For lighter shades use the following reducing paste :—

Reducing Paste B.G.

775 parts Z. Paste B.G.
225 ,, gum Senegal 30 per cent.

1000

(*b*) For Colours in the Uncrimped Black Stripes.

B. Resist White G.T.

200 grms. precipitated chalk.
50 ,, sulphite of potash 90° Tw.
50 ,, acetate of soda.
5 ,, Ultramarine blue.
345 ,, water.
350 ,, 6 per cent. tragacanth thickening.

1000

Grind well.

Z. Paste G.T. (Colours only) Standard.

200 grms. zinc oxide.
25 ,, glycerin.
180 ,, water.
340 ,, 6 per cent. tragacanth thickening.
30 ,, turpentine.

775

Grind well.

B. Colours G.T. (for Uncrimped Figured Resists on the Plain Black Ground).

Except that Z. Paste G.T. Standard replaces Z. Paste B.G. Standard, these colours are identical with those immediately preceding, namely, the B. Colours B.G. Being thickened with gum tragacanth, they offer no resistance to the penetration of caustic soda into the cloth, and consequently they do not impede its mercerisation like the B.G. colours, which are thickened with British gum. Both groups of colours prevent the development of Aniline black by reason of the zinc oxide they contain.

A pattern consisting of alternate blue and white crimp stripes, having between each stripe a floral pattern in, say, red, pink, blue, yellow, green, and white, the whole being on a black ground, is produced by the following sequence of operations :—

(1) Print the blue and white stripes in B. Blue B.G. and B. Resist White B.G., and the rest of the pattern in B. Red G.T., B. Pink G.T., B. Blue G.T., B. Yellow or Gold G.T., B. Green G.T., and B. Resist White G.T. Dry.

(2) Steam for one hour. This may be omitted, but it improves the fastness of the colours. The steam must not be too moist.

(3) Pad through prussiate Aniline black in the usual manner for resist black styles. Dry quickly, but not too hard.

(4) Steam for from 2-4 minutes in the rapid ager, and pass through gaseous ammonia.

(5) Pad through caustic soda 63° Tw. Squeeze out excess of liquor and allow to lie a few minutes.

(6) Wash, in the rope form, in plenty of running water.

(7) Sour in sulphuric acid ¼° Tw. Wash in water (optional).

(8) Wash in water containing a little ammonia ; hydro-extract and dry up.

Goods printed according to any process of reserving Azoic colours under Aniline black may be converted into crepons by running a stripe over them in thick British gum and, after drying, padding in caustic soda as above ; or, more simply, by printing them directly with caustic soda. In neither case is it possible to obtain the crepon stripes in either white or single colour, or in register with the reserve colours ; they fall indiscriminately over pattern and ground, and take the colours of each. The same remarks apply to all styles in which the crepon stripes are printed as a cover.

Other methods of producing Direct colour resists under Aniline black for crimping are of little technical value : neither acetate of soda, acetate of zinc, acetate of magnesium, caustic soda, nor alkali carbonates yield results at all comparable with the zinc oxide resists. In each case the colours are duller and weaker, no matter how they are applied.

Vat and Indigosol resists under Aniline black, Rapidogen and Vat colour resists under Indigosol grounds, Vat colour discharges on Azoic colour grounds, and all combinations of these colours, lend themselves perfectly to crimping with caustic soda.

Crimped metallic stripes are exceedingly effective so far as appearance is concerned, but they require care in their execution, otherwise the caustic soda is liable to saponify the oil and resin (varnish) with which they are fixed. To avoid this as much as possible, the printed goods are allowed to hang longer

than usual in order thoroughly to harden the varnish ; they are then calendered to burnish the metal, and finally padded through caustic soda and washed off without undue loss of time.

The best kind of fabric for crepon printing is one with more warp than weft, the most pronounced crimping of the stripes being the result of the contraction of the cloth in the direction of its length.

PART VIII.

FINISHING OF PRINTED CALICOES.

FINISHING OF PRINTED CALICOES.

FINISHING—the last stage in the production of a calico print—is a very important operation, since upon the quality of the finish depends in many cases the market value of the goods. The sole object of finishing is to give what is considered to be an attractive appearance and handle to the printed fabric. As to what constitutes an attractive appearance is a matter of opinion, and one better left undiscussed here; for many merchants require the same cloth, printed with the same pattern and in the same colours, to be finished in different ways, according to the individual taste of their customers in the various markets for which the goods are intended. Hence, taking into account the hundreds of different sorts of cloth in general use, it is obviously impossible, in a work of this size, to treat the subject of finishing on anything like definite lines; and it would be no less so even if a particular material were always given the same finish, because the methods and materials employed to attain identical results must be varied according to the condition in which the finisher receives the goods. For instance, goods printed in pigment colours, and steam colours thickened with starch or flour, are generally stiffer and harder than dyed goods and those that have been printed in gum-thickened colours. Consequently they must be treated differently in finishing if they are all to have the same ultimate "feel" and appearance. In some cases the stiffness, if undesirable, may be removed by re-soaping the cloth, or by steeping it in a weak infusion of malt for several hours, followed by a good washing; but this is not always feasible, especially if the colours are only moderately fast, and in such cases the finisher has to impart the necessary softness by other means. In like manner also the extra stiffening and other operations connected with the production of a particular kind of finish have to be modified in the course of working, in order to obtain uniformity in the feel, gloss, weight, and appearance generally of the various lots of one cloth printed with the same, or same class of, pattern, but in an assortment of colours which have been applied by different methods and thickened with very different materials.

From the foregoing it will be evident that the business of the finisher can only be learned by experience, and that successful finishing can only be accomplished by employing such processes as experience, guided by the evidence afforded by a critical examination of the goods to be treated, shows to be best calculated to yield the required result. Moreover, finishing, although, like engraving, an integral part of calico printing, is yet a separate and distinct trade, with a literature of its own. Hence, more than a brief reference to and outline of the principal processes of finishing will not be attempted.

Finishing comprises the operations of stiffening, clearing, drying, stretching, calendering, embossing, measuring, and making up into attractive packages.

(1) **Stiffening** is effected by two different methods—

a. Padding in starch or other pastes (Mangle finishes).

b. Back starching.

Beyond the employment of suitable pastes, the first method is identical with the padding of dye liquors, and is performed in machines of similar construction (see Plate XV.).

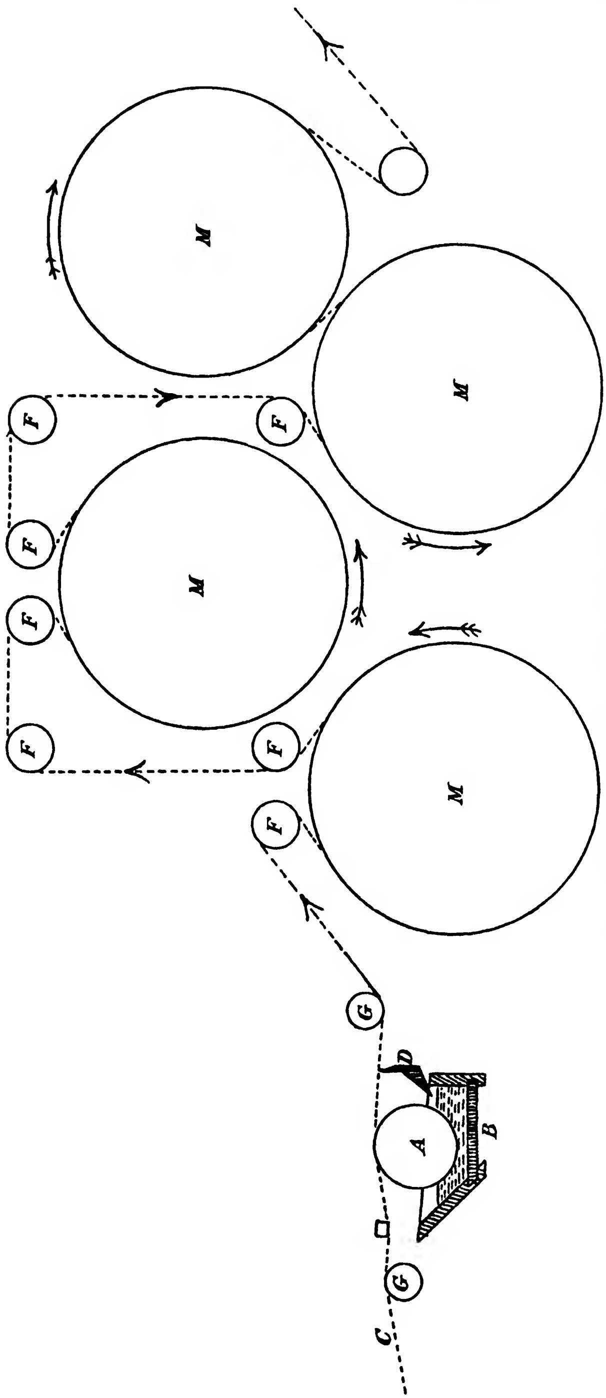
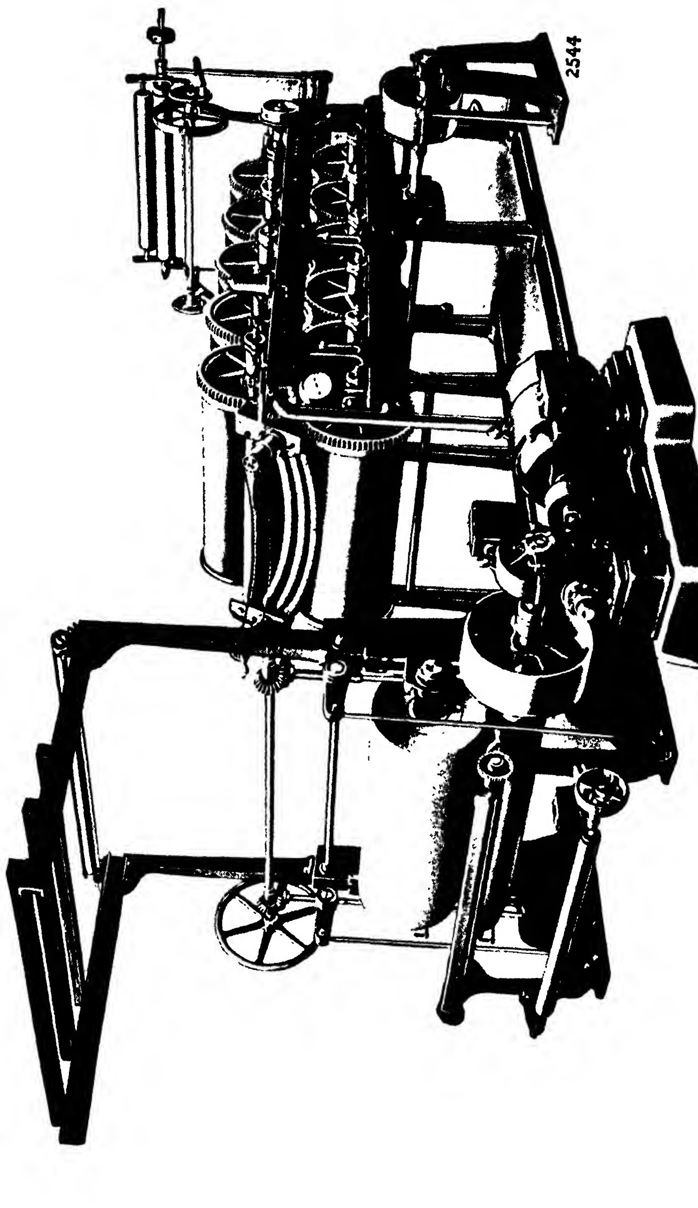


Fig. 87.—Section of back starching arrangement.

In "back starching" the procedure is different in every respect, inasmuch as the goods do not pass through the stiffening paste, but have it applied to their unprinted sides by means of a roller, the lower half of which works in the paste, while the upper part comes into contact with the back of the cloth as it travels forward through the machine. Excess of starch is scraped off the cloth by a brass doctor placed immediately behind the starch roller. Fig. 87 will explain the mode of action of a back starcher.

A is the starch roller, B the box containing starch paste, C the cloth, printed side uppermost, D the doctor, G G two adjustable guide rollers, F F skeleton guide rollers, M M large drying cylinders. The drying of the cloth is so arranged that the starched side does not come in contact with the cylinders until it is sufficiently dry not to mark off. The brass doctor D is adjustable, so as to allow of a greater or less amount of starch remaining on the goods as required.



Finishing Range.

Most printed goods that are starched are treated on a back starcher in order that the brilliancy of the colours may not be impaired by the presence of a film of semi-opaque starch. For transparent finishes, they are usually padded in solutions of gum, soluble starch, or soluble salts.

A variety of starches is used, differing in the nature of the pastes they give when boiled. For some purposes a firm, stiff paste is best, whereas for others the softer and more gummy the consistency of the paste the better. By a suitable choice of starches all degrees between the two extremes may be obtained. As a rule, potato starch and sago flour are preferred, but wheat starch is also used, and besides pure starches there are many special finishing starches on the market.

For transparent finishes, the stiffening agents used are chiefly dextrine, soluble starch, common salt, and Epsom salts, the last chiefly in combination with other ingredients.

China clay is extensively employed in all branches of starching to increase the weight of the goods, and to fill up the interstices in low-grade fabrics. Far too much attention is paid to the weighting and filling of cotton fabrics, and, so far as the home trade market is concerned, it is a questionable policy to give the goods an appearance of solidity that they are far from possessing: the first wash removes the adulteration, and shows up the poverty-stricken quality of the cloth; and as no one wants to buy China clay and starch for calico, the exposure of the deception results in the loss of a customer if the goods have been originally purchased for the apparent quality of the material. In the case of goods that are not intended or expected to stand washing, weighting and filling may be used without drawback; and in certain styles of decorative work, such as temporary hangings and upholsterings, they are an advantage, since they allow of cheaper material being used for purposes which more expensive goods would serve no better. China clay is always employed along with starch and not with any other thickener.

Auxiliary Products used in Starching or Stiffening.—Amongst other adjuncts of the finisher are softening agents and various blueing substances. The former consist for the most part of soap, tallow, Turkey-red oil or glycerine, and sometimes glucose. Various hygroscopic salts—*e.g.* calcium chloride, magnesium sulphate, zinc chloride—and antiseptic bodies are also employed to impart softness and weight, and to prevent the formation of mildew. For blueing purposes artificial Ultramarine is generally preferred, but occasional use is made of the soluble artificial dyestuffs of the Basic and Acid groups. The object of blueing is to neutralise the unpleasant yellow tint of white grounds—a tint that is always noticeable before finishing. The blue is applied in several ways according to circumstances. Generally it is mixed with the stiffening, but sometimes with the clearing liquor, and sometimes it is applied in a separate operation.

(2) **Clearing.**—This process simply consists in passing the goods through a dilute solution of bleaching powder and then, without washing, drying them directly over steam-heated cylinders. In some cases the goods are passed through a steam box before drying, but this is usually done before the finisher receives the goods. If the goods are only very slightly tinted, the bleaching liquor may, at times, be added to the starch paste used for stiffening.

(3) **Drying.**—After starching or otherwise stiffening, printed calico is usually dried over cylinders. If, however, it has lost too much width in process, it is dried a second time over a machine specially designed both to dry and stretch it out to the required width. This machine, known as a stenter, consists essentially of a long horizontal frame of iron, along each side of which an endless chain constantly travels. On entering the machine, the cloth is gripped at the

selvedges by pins or clips attached to the two endless chains, which, for a certain predetermined distance, gradually recede from each other, thus stretching the cloth breadthwise. At the same time the cloth is damped on the under side by steam, so as to increase its elasticity. When the desired width has been reached the chains run parallel to each other ; and the cloth, now held at the full stretch by the clips, and still travelling forward along the remaining length of the machine, is dried by the strong heat of a forced draught of hot air applied to its under side—a heat which not only dries but sets the cloth, and prevents its subsequent shrinking to the narrower width when it is finally released from the grip of the chain clips.

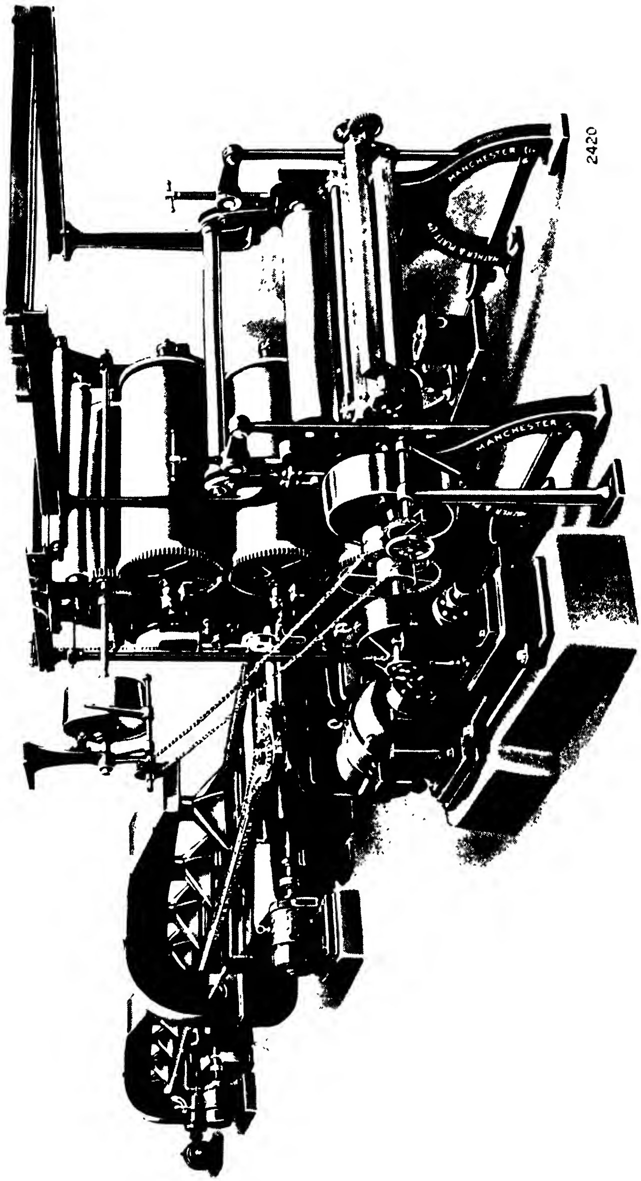
In certain styles, notably in muslins, the finish is almost, if not quite, as important as the cloth itself. Mercerised muslins are usually finished soft, being as a rule simply passed through water containing a very little Turkey-red oil, then stretched and dried to width over the stenter, and finally calendered lightly to smooth them down. Starching is avoided as much as possible, as it tends to flatten the silky lustre of mercerised goods.

On the other hand, the characteristic "Batiste Finish" on muslins is obtained in quite another way, and depends upon the previous stiffening of the fabric, combined with a special method of stretching and drying. Starched muslin dried over any of the ordinary machines or stenters has a hard, boardy feel, is rigid, and inelastic and rough to the touch. In order to overcome these defects it is dried and stretched over a specially constructed stenter known as a Jig Stenter (Plate XVI.). In this machine the clip chains travel forward along the frame with a to and fro movement in the direction of their length, each chain advancing and retreating in turn so that the cloth gripped between them is stretched by the constant backward and forward movement of its selvedges. The arrangements for damping and drying are exactly like those in the ordinary stenter ; in fact, the Jig Stenter is generally designed to work at will as an ordinary stretching machine, the Jig Motion being simply an extra movement. The effect of stretching and drying or Jigging the cloth in this manner is to cause the warp and weft threads to rub against each other, and thus to prevent them sticking together when the stiffening is dry. Batiste finished muslins have a soft, full, springy feel, something like that of silk, but without its lustre ; they are perfectly free from hardness, and possess a certain amount of elasticity which enables them to drape well without falling into clinging folds.

(4) **Damping.**—After stiffening with starch, dextrine, gum, etc., the goods are by no means in a fit condition for delivery ; they are hard, rough, often boardy, and frequently so papery in texture as easily to be torn. In order to develop the qualities of a finish, or to impart a mellow feel to the goods, the stiffened pieces must be subjected to one or more of the further operations of calendering, Schreinering, beetling, breaking, or softening—operations which cannot properly be carried out unless the pieces are first "conditioned"—that is, brought into a suitable state of humidity, either by exposure to a damp atmosphere until they have absorbed sufficient moisture, or by passage through a damping machine in which they are sprayed with water in a finely divided state. This question of damping receives less attention, in general, than it merits ; in many cases the moisture content of stiffened pieces is the controlling factor in the success or otherwise of a finish.

Conditioning is effected before calendering in two types of machines, viz. Brush Damping Machines and Spray Damping Machines. Many models of both are in use.

In the Brush damping machine a cylindrical brush revolves at a high speed in contact with water in a trough below and, thus, throws off a shower of fine



High-speed Stentering Range, with jigging motion.

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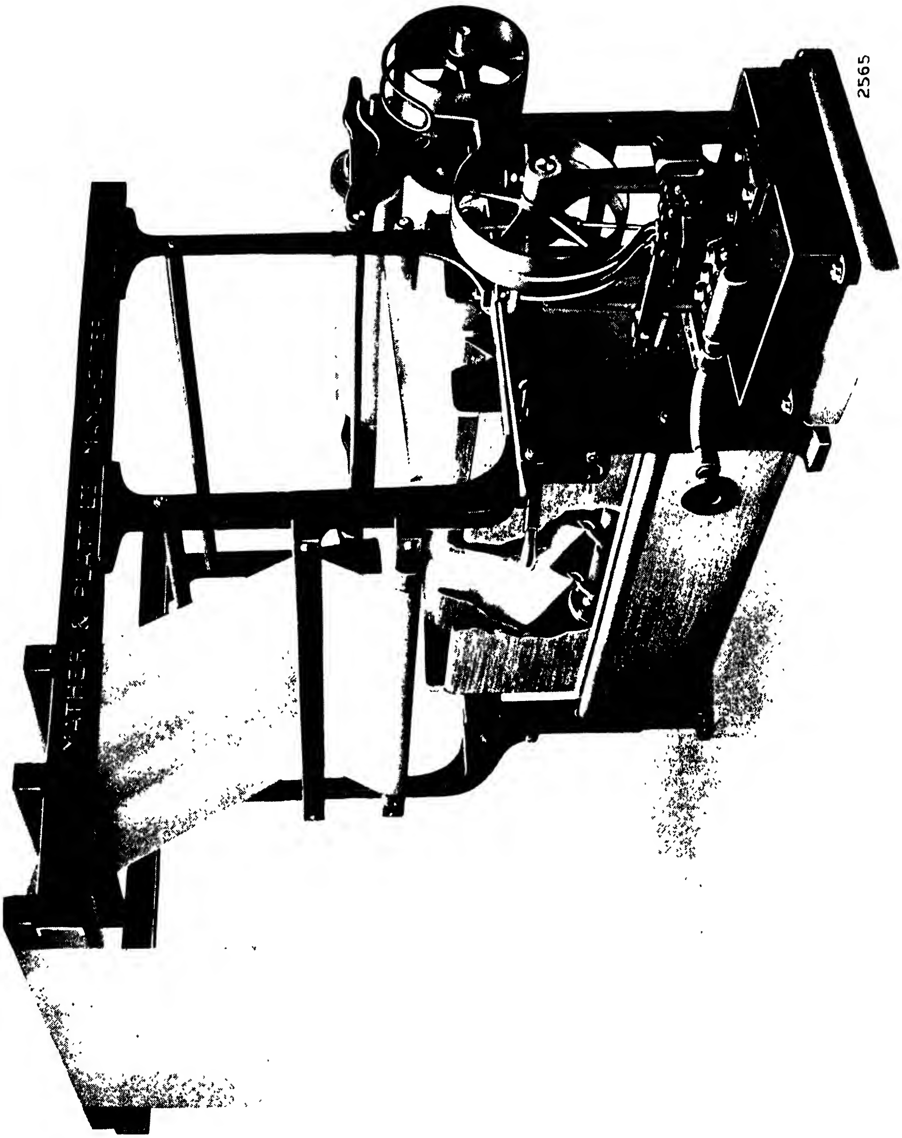

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drops, which spray the under side of the cloth as it passes quickly above the trough. The brush is made of bristles or copper spikes, and the damping of the cloth is regulated by raising or lowering the level of the water in the trough by means of an adjustable overflow. Brush and water trough are contained in an open-topped box above which the cloth travels, and further regulation of the damping may be obtained by varying the width of the opening at the top of the box, hinged lids being provided which may be opened or closed according to the degree of damping required. The cloth is drawn across the opening of the box by the usual draw rollers, is guided along its course by guide rollers, scrimp rails, and tension rails, and is, finally, plaited down or batched on a wooden centre.

Spray damping differs from brush damping only in the means whereby the spray is produced. In place of a revolving brush impinging on the surface of water, use is made of a series of nozzles, arranged at suitable intervals along a common supply pipe, as shown through the cut-away portion on Plate XVII., which also illustrates the latest improvements in the construction and general disposition of damping machines. The principle on which the nozzles work is that a jet of water discharged under considerable pressure against an inclined disc becomes atomised into an exceedingly fine spray. The water in the form of the finest possible cloud-like spray, entirely free from drops, is delivered to the cloth as it passes forward across the top of the enclosing box at an appropriate distance above the nozzles. The damping is controlled by hinged shutters fixed on the box, as described for brush damping (see also Plate XVII., in which the shutters are clearly shown). An automatic device shuts off the sprays as soon as the machine stops, and thus provides against over-damping of the cloth if, for any reason, the machine is suddenly brought to a standstill. Owing to the fineness of the nozzles it is advisable to use filtered water, which is best supplied to the nozzle feed pipe, under constant pressure, by means of a three-throw pump.

Spray damping is usually preferred to brush damping on account of its uniformity and its freedom from drops.

(5) **Calendering.**—A calender is a machine having heavy cylinders revolving, when in work, in contact with each other, so that cloth passing between them is smoothed and glazed by their pressure. The degree of glazing depends on the amount of pressure put upon the cloth.

Ordinary calenders consist of an iron bowl in the centre, with two paper or compressed cotton bowls above and below. The iron bowl is hollow, so that it can be heated by steam or gas, a contrivance which is required for certain finishes.

When a very high glaze is required, use is made of the Friction or Swissing Calender. This machine consists of one hollow chilled iron bowl, arranged to be heated by steam or gas, one paper bowl above it, and above that a second and smaller iron bowl, which works at a higher speed than the two lower ones, and thus causes friction. The action of the friction-bowl results in the production of an exceedingly brilliant glass-like glaze, which can be controlled either by reducing the speed of the bowl in question or by decreasing its pressure on the fabric. Friction calenders of five or more bowls, adjustable for different styles of finishing, are also made (see Plate XVIII.).

In the embossing calender (for producing the *moiré* finish) a variety of figures are impressed on the cloth by an engraved steel roller working between two paper bowls under heavy pressure. The engraved bowl or roller may be heated from inside by gas or steam according to requirements.

The well-known "silk or Schreiner" finish is obtained by embossing mercerised cloth with a series of fine oblique lines in a machine of similar

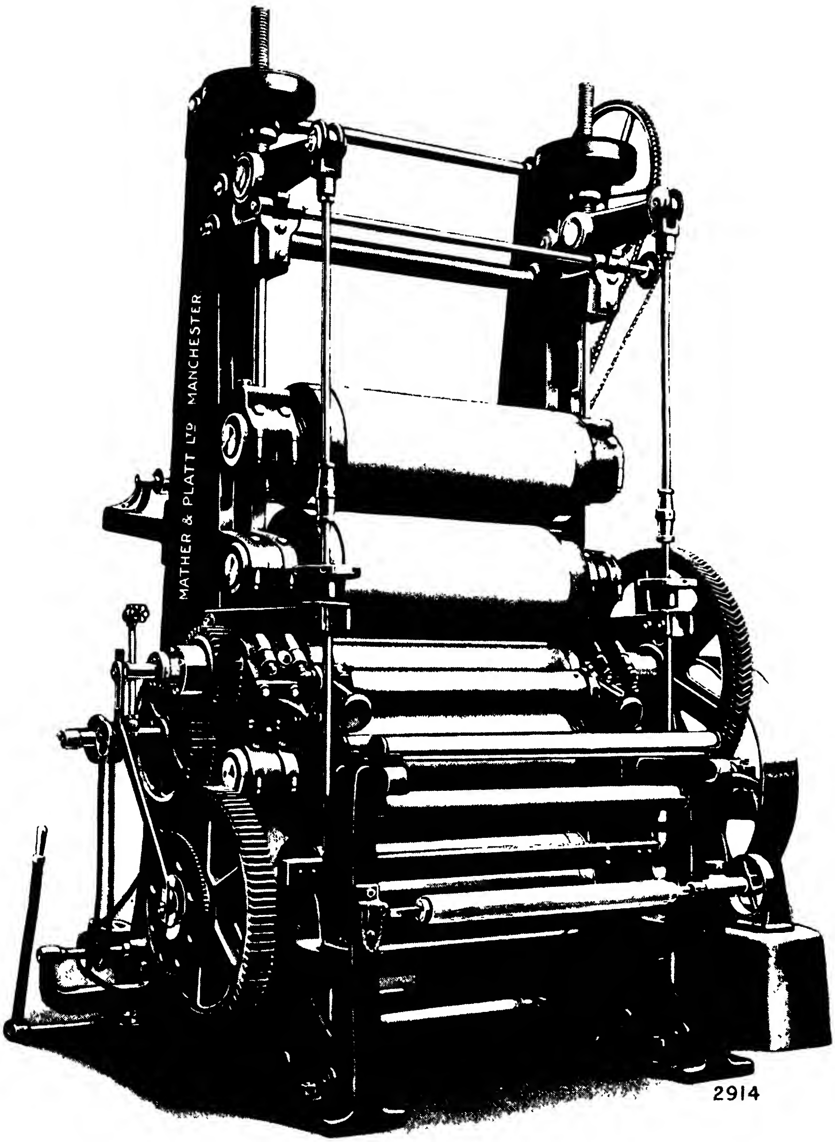
description but rather different construction. The Schreiner Calender (see Plate XIX.) consists essentially of an upper, highly polished steel bowl, engraved over its entire working surface with very fine oblique or "slashed" parallel lines, and a lower and larger pressure bowl made of compressed cotton or paper. The upper engraved bowl is provided with gas heating apparatus and is mounted and revolves in fixed bearings which form part of the heavy rigid framework of the machine and are fitted with bronze steps and are water-cooled. The bearings of the lower bowl are carried on the rams of hydraulic cylinders, by means of which the bowl may be raised or lowered in or out of contact with the upper bowl. In operation the lower bowl exerts and maintains an even and constant pressure against the upper bowl, the pressure being applied to the rams by a hydraulic pump working in conjunction with a hydraulic accumulator which controls automatically the pump delivery. The upper bowl is coupled directly to the motive power and drives the lower through frictional contact. The engraved steel roller carries up to 256 lines to the inch, and when these are impressed on the cloth under great pressure they form thereon a multitude of minute and highly glazed ridges, from the sides of which a large amount of light is reflected. Embossed in this manner the fabric acquires a beautiful soft sheen, totally different from the brilliant glaze produced in the swissing or friction calender. Different qualities of sheen may be obtained by replacing the plain line pattern of the Schreiner finish by various figured patterns such as *moiré*, watered, cross-hatched, honeycomb, or other delicately engraved close-set design.

For producing embossed patterns in higher relief than can be obtained by passing the goods between one dead smooth and one engraved cylinder, the cloth is passed between two engraved rollers, the one carrying the design in relief, the other with the design in intaglio. Either one or the other may be heated as required.

In addition to its employment for the Schreiner finish and its allied styles, the finer and more delicate sort of embossing is largely used for the production of figured effects on heavily surface-starched bookbinding cloth. In this case the cloth is frequently weighted and filled with China clay or other plastic substances mixed with thick starch paste, which is coloured to the desired shade by the addition of dyestuffs. The coloured paste is applied either by printing or in a back starching machine, and, after drying, the goods are simply calendered and embossed without any further treatment for the fixation of the colour.

Watered or *moiré* effects on the back (or face) of various classes of calico may also be obtained by passing two pieces at once through the calender, back to back, or face to face, as the case may be. The rough surfaces presented by the warp and weft threads of each of the sides in contact act in much the same manner as engraved rollers towards each other, and, under great pressure of the calender bowls, they mutually emboss each other, with the production of an ever-varying "watered" or *moiré* effect. The cause of the watering is due to the crossing of the respective threads of the two pieces, whereby they become more flattened in some parts than in others, and consequently more highly glazed, in which condition they naturally reflect light unevenly. The same effect in a repeating pattern is obtained by engraving an embossing roller with two distinct series of fine lines, the one crossing the other at various angles according to the kind of watering required.

A modification of this process, known as "Chasing," consists in passing two or more folds or thicknesses of the *same* piece of cloth one or more times through the nip of the bowls before the goods finally pass out of the calender, *i.e.* two or more folds, in contact, are calendered together. To this end the



5-Bowl Finishing Friction and Chasing Calender.

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cloth, after its first passage through the calender, is immediately conducted from the top bowl to one or other of the nips through which it has already passed, and thus re-enters the machine along with a fresh portion of the same cloth which is passing through for the first time. The re-entry is effected by threading the cloth over auxiliary guide rollers—chasing rollers—situated behind the bowls, and may be repeated as often as desired by increasing the number of chasing rollers. In some classes of finish the cloth is passed through the nips and " chased " round in multiple folds seven times. For specialities of this description nine- or ten-bowl calenders are used ; for ordinary chasing, the five-bowl calender illustrated in Plate XVIII. is sufficient for most demands. Chasing has the effect of rounding off the threads of the cloth and, as in the case of *moiré* effects, the threads of the superposed layers of cloth emboss each other, thus imparting a lustrous, thready appearance to both sides of the fabric.

In what is known as a " chesting calender " there are at least five cylinders or bowls, the middle one being of iron and hollow, so as to be heated by gas or steam, the extreme top and bottom bowls being also of iron, with a compressed paper bowl between each of them and the centre bowl. In chesting, the cloth passes continuously between each pair of bowls, and instead of running out of the machine as it leaves the last, it is wound on the uppermost iron bowl, which is specially arranged to allow for the increasing pressure due to the increase in its size (or diameter) brought about by each additional thickness of cloth wound round it. When a sufficient quantity of cloth has been wound on, no more is fed into the machine, and the top bowl, with its load of cloth, is then revolved under constantly increasing pressure until the desired result is judged to be attained.

At this point the direction of the chesting bowl is reversed, and the cloth transferred from it to a batching roller ; whilst batching, the pressure on the cloth is relieved, only sufficient being retained to prevent the chesting bowl from overrunning the batching apparatus. In modern machines a special brake motion is provided for this latter purpose. Chesting is never employed for printed goods, and therefore calls for no further description.

Another method of giving a gloss, and at the same time a thick, silky feel, to sateen cloth, etc., is that known as " Beetling." A great variety of Beetle finishes are produced, but they all depend upon the principle of giving heavy elastic blows to the cloth with great rapidity. In order that each part of the cloth may be uniformly hammered the goods are beamed on heavy, slowly revolving rollers of iron, situated immediately beneath a row of beaters or beetle hammers. In the old form of machine these beetles consist of stout balks of timber, raised and allowed to fall on the cloth by means of cams which alternately engage with and release a projecting peg fixed at the back of the hammer. In modern machines these simple appliances have been replaced by leather-faced beetle hammers, actuated by steam power through the medium of cranks and connecting rods, and provided with springs to increase the elasticity of their blows. The massive iron beams or rollers upon which the goods are wound revolve slowly during the whole process of beetling, so that every square inch of the cloth receives identical treatment. The various finishes are obtained by varying the duration of the hammering, the thickness of the stiffening mixtures previously applied to the fabric, and by other methods, such as winding on two pieces back to back, etc.

In all operations connected with starching, calendering, embossing, and beetling it is highly important that the cloth should pass through the processes at the full open width, without a crease. To ensure this condition brass expanding rollers, expanding cones, and corrugated brass or hard-wood scrimp

tension rails are placed in front of all machines used in finishing. In starching and stiffening generally a crease or scrimp or double edge merely gives rise to unsatisfactory and irregular work, and is not, as a rule, likely to result in any damage to the fabric. But in calendering, embossing, and beetling, where the cloth is subjected to enormous and sometimes grinding pressure, the least crease constitutes a grave source of danger, and in the bulk of cases results in a more or less extensive tear. Apart from injury to the fabric, however, the presence of a crease or double-over selvedge invariably damages the delicately engraved rollers of the Schreiner calender; and as the re-engraving of these involves considerable expense, it is obvious that the utmost care should be taken to avoid exposing them to risks at the hands of careless or ignorant workmen.

After finishing, the printed goods are plaited in folds of a definite length on special Plaiting and Measuring Machines, which can be regulated to lay the cloth in regular folds of either a yard or a metre, or fractions of these standards. All that then remains to be done is to cut off a certain number of folds, make them up into attractive packages (in England generally containing 30 yards of cloth), arranged so that the quality of the article can be easily seen and examined, ticket the packages with distinguishing tickets denoting the pattern, quality, class, width, and length of the cloth, and any other particulars required by the market, and finally to bale them up and consign them to their destination.

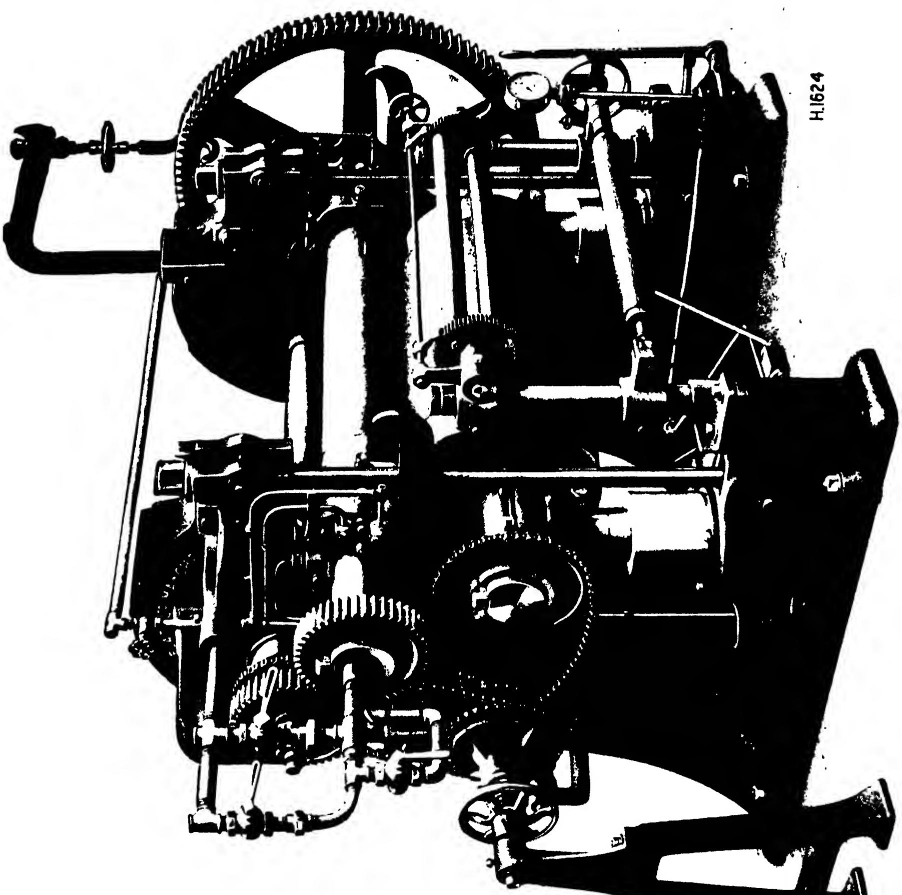
For fuller particulars relating to the production of the scores of finishes in general use, the reader is referred to the standard works on the subject, namely:

Traité des Apprêts; Depierre, 2nd Ed., 1894 (Baudry, Paris).

Chemistry and Practice of Finishing Cotton Goods; Bean and M'Cleary, 1905.

Finishing of Textile Fabrics; Beaumont, 1909.

The Bleaching and Finishing of Cotton; Trotman and Thorp, 3rd Ed., 1927 (Griffin).



Hydraulic Schreiner Calender.

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PART IX.

WOOL PRINTING.

WOOL PRINTING.

COMPARED with the printing of cotton, that of wool is a simple matter in so far as the fixation of dyestuffs is concerned. For most dyestuffs, the wool fibre has a much greater affinity than cotton, so much so indeed that by far the greater number of them are sufficiently fixed on wool without the employment of any mordant whatsoever. This is notably the case with the majority of the Basic coal-tar colours, which, when applied to cotton, can only be fixed as tannin or chrome lakes, or by means of albumen. On cotton, too, the Acid colours cannot be satisfactorily fixed at all, whereas for wool they constitute the most valuable group of colouring matters, since they yield exceedingly bright and, for most purposes, sufficiently fast colours. On wool, however, as on cotton, the faster shades are produced by means of the Mordant dyestuffs, which are applied in much the same way as to cotton. In wool printing the mordant colours are only used when fastness is of more importance than brightness, or when the shade required can be obtained from them more readily than from other classes of colouring matters. To some extent the Direct colours are also printed on wool, but their application is limited, since they are inferior in brightness to the Acid and Basic colours. The chief use of Direct colours in wool printing is for dyeing ground shades that are afterwards to be discharged with stannous chloride or hydrosulphite.

The natural affinity of wool for colouring matters is greatly enhanced by preparing it in tin salts, and by acting upon it with chlorine. This latter process was invented by John Mercer, who found that in chlorinated wool the depth of the colours was greatly increased, sometimes even to double that otherwise obtainable. Only by chlorinating the wool is it possible to bring about the full development of most colours, and thus to ensure the utilisation of the dyestuffs to the best advantage.

Before being printed, the woollen goods require bleaching in either sulphurous acid gas, bisulphite of soda, or hydrogen peroxide. The last two methods are most commonly employed in printworks.

In the Bisulphite Process the goods, after properly scouring in alkaline baths, are well washed and squeezed, and then passed alternately through baths of bisulphite of soda and hydrochloric or sulphuric acid; or they are slop-padded in bisulphite, and steamed for a short time. After bleaching, the goods are prepared in stannate of soda or chloride of tin, followed, except for very light patterns, by a run through a weak, acidulated solution of bleaching powder. They are then thoroughly washed, squeezed, and dried up ready for printing. There are several methods both of chlorinating and preparing in tin, and sometimes the sequence of the operations is reversed. In some cases the tin preparation is omitted, and the pieces chlorinated and bleached in a continuous manner by being passed successively through baths of bisulphite of soda, bleaching powder, and sulphuric acid.

For delaines (*mousseline de laine*), which are the fabrics mostly used for printing, the following process of preparing the goods has given good results :—

a. SCOURING.—(1) Wash the goods in the rope form in hot water (60° C.) for ½ hour.

(2) Soap with 10–15 per cent. (on the weight of the goods) Marseilles soap for ½ hour at 60° C.

(3) Wash well in water, hydro-extract, and bleach.

b. BLEACHING.—(1) Pass the goods in the open width through a solution composed of—

1 part peroxide of hydrogen (10 vols.) ;
4 parts water ;
and sufficient ammonia to make slightly alkaline.

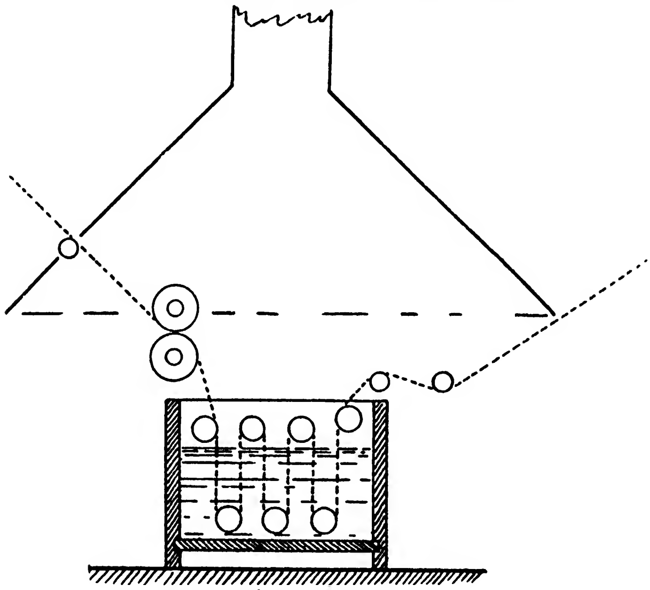


FIG. 88.—Chlorination beck.

After passing through this solution the goods are rolled up in the wet state and allowed to lie 24 hours ; they are then washed and passed through a solution of bisulphite of soda, the concentration of which varies according to the discoloration of the material.

(2) BISULPHITE BATH.

1 part bisulphite of soda 70° Tw.
2–8 parts water.

Roll up again in the wet state and allow to lie a few hours ; then pass directly through sulphuric acid 2°–2½° Tw., and finally wash thoroughly, hydro-extract, or squeeze out the excess of water.

Woollen goods may also be bleached with sodium peroxide and with potassium permanganate but, for printing purposes, the results are not better than those obtained as above.

c. CHLORINATING.—This process is carried out in a wooden or stone cistern furnished with guide rollers and squeezing bowls, and capable of holding about 2500 litres of liquor. Above the cistern or beck a hood is fixed to carry off the fumes of chlorine liberated during the operation. (See fig. 88.)

The chlorinating beck is charged differently according to the style of work in hand. Thus—

(1) For White Grounds.	For Dark Blotches.
2000 litres	2000 litres water.
12 ,,	20 ,, bleaching powder sol. 10° Tw.
8 ,,	25 ,, hydrochloric acid 32° Tw.

The goods pass through these solutions in from 15–20 seconds, and for each piece the baths are replenished by adding—

For White Grounds.	For Blotches.
¾ litre	2½ litres bleaching powder sol. 10° Tw.
4½ litres	1½ ,, water.
½ litre	1½ ,, hydrochloric acid 32° Tw.

(2) Wash well in plenty of water, and dry up through a dilute solution of glycerine on a stentering machine. The presence of a little glycerine enables the fibre to absorb the colour better, and is generally an advantage, especially during the subsequent steaming of the printed goods.

d. Tin Preparation.—(1) Pass the goods twice through stannate of soda at 10° Tw. Squeeze, and then pass at once through—

(2) Sulphuric acid 2° Tw., or hydrochloric acid 2° Tw.; wash well and dry.

Another method of preparing wool is first to pass through stannate of soda 10° Tw., then through hydrochloric acid 2° Tw., and finally through bleaching powder solution 1½° Tw., followed by a good washing and drying. The first method described, however, is generally considered to give the best all-round results.

If, during the course of chlorinating, the wool is observed to turn yellow, its speed through the liquor must be increased, or the strength of the liquor must be diminished until the defect is rectified. It is necessary also to have always an excess of acid in the chlorinating liquor, otherwise apparently satisfactory goods will develop yellow stains, extending throughout their whole length, in the steaming process. To guard against any risk of this happening in the case of white ground prints, it is a common practice to prepare the goods in stannic hydrate only, omitting the chlorine treatment altogether. In most cases, however, it is usual to give the pieces a treatment in bleaching powder, whether for white grounds or not; and even when the chlorinating, as such, is omitted, it is not infrequently the custom to add about ½ litre of bleaching powder solution 4° Tw. to the acid bath used in the tin preparation (½ litre, that is, for every 50 yards passing through the acid).

The stronger the chlorination, the greater the affinity of the wool fibre for Acid colours; but it is important to note that the stronger the treatment, the yellower in shade and the harder to the touch does it become. According to Pokorny (*Journ. Soc. Dyers and Col.*, 1908, p. 114), the chlorination of wool decreases its affinity for Basic colours, whereas the treatment with strong bisulphite of soda increases the affinity of wool for these colours.

Printing and Steaming.—The printing of woollen piece goods is performed in the usual manner, either by machine or by block. Practically all wool colours are suitable for machine printing; but in block printing, care must be taken to use only such colours as require considerable heat for their fixation on the fibre, or of which the fixation can be retarded by the addition of certain ingredients, such as stannous chloride, stannic chloride, tungstate of soda, bisulphite of soda, and phosphate of soda. The less easily a colour dyes wool in the cold, the more likely is it to equalise well at the repeats of a block printed pattern in steaming.

Similarly, colours for which wool has great affinity are less suitable for block printing, because they become fixed on the fibre almost at once, and thus render impossible the merging of the colour of one repeat into that of the repeat next applied. Such colours invariably yield uneven results, whereas those which are only developed and properly fixed in steaming produce the utmost degree of uniformity to block printing by hand. These remarks apply more particularly to the printing of blotches and large spaces of colour—a style of work in which a smooth, level print is of the greatest importance. For small patterns in many colours, it is unnecessary therefore to pick and choose, since the repeats of such patterns are usually arranged to be invisible under any condition.

With respect to machine printing, there are also several precautions to be observed if the best results are to be secured. For heavy patterns and all blotches the rollers must be deeply engraved, and, in general, delicate engraving of any sort is to be avoided. The cylinder of the printing machine ought to be lapped more thickly than for calico printing, and the blanket must be as soft and thick as possible. It is very important to dry the printed pieces at a moderate temperature, so that, as they emerge from the drying apparatus, they are only just dry or, better, just slightly damp. In some cases, even, the goods are plaited down between grey cloths, without any other drying than is obtained in this way, though usually they are passed through the ordinary hot-air apparatus, at a temperature adjusted to fulfil the required conditions, namely, gentle drying, with the retention of a trace of moisture.

In *steaming*, the presence of moisture is absolutely essential. The degree of humidity of the goods exercises great influence on the fixation, regularity, and brightness of the colours: if goods are not sufficiently damp, the fixation of the colours is imperfect, and they wash out a good deal, staining the surrounding parts of the cloth; conversely, if the fabric is too damp, the colours run, and the sharpness of the impression suffers in consequence. In general, the required degree of humidity is obtained by wrapping the printed goods in damp greys containing from 5–15 per cent. of moisture, according to thickness or dryness of the woollen material to be steamed.

The steaming operation is usually effected, without pressure, in a cottage steamer; but a wooden box or a brick chamber may be utilised so long as the steam employed is moist. The moisture is introduced by blowing the steam through water contained in a small tank situated at the bottom of, or beneath, the steaming box, and suitable arrangements are made to prevent the pieces being splashed. The moister the steam, the deeper and brighter the resulting colours; too much moisture, however, is to be avoided, lest the colours run, and spoil the whole print. The pressure ought never to exceed that corresponding to a rise of 2–4 inches in a small water manometer attached to the steaming apparatus. The duration of steaming depends upon the weight, intensity, and nature of the colours printed; darker colours require a longer treatment than light ones. In some instances, notably for delicate floral patterns, the goods are steamed twice, being damped if necessary between the two operations.

The treatment of printed woollen fabrics after steaming is much simpler than that of calico prints. Patterns on woollen goods are always produced either by direct printing or by discharging dyed grounds, so that there are no dyeing, fixing, or clearing processes to complicate the after-treatment. The usual treatment after steaming is simply to wash the goods in the loose rope form in a copious supply of fresh running water.

The first wash may sometimes be followed by a second in warm water, but, generally speaking, a thorough wash in cold water is sufficient for most purposes.

During the washing, provision must be made against the fixation of loose

colour on the white parts of the pattern. With cold, hard water this rarely occurs if the steaming has been properly carried out, but if warm water or very soft water is used it is advisable to add a little chalk to the water in the washing machines. This frequently precipitates the washed-off colour, and thus prevents its fixation on the cloth.

After washing, the goods are hydro-extracted, and finally dried on the stentering machine. Soaping is rarely employed for printed woollens, except where the whole of the colour combinations is got up in fast Mordant colours.

Colours Used in Wool Printing.

Owing to its strong attraction or affinity for the majority of colouring matters, wool may readily be printed with every type of dyestuff except Indigo, Sulphur and Azoic colours and a few special colours prepared for acetate-silk. Indigo and Sulphur colours involve the use of strong caustic alkalies, which destroy wool, and the Azoic colours, although they demand an almost negligible quantity of caustic soda for their production, present other drawbacks which have, hitherto, prevented their satisfactory employment in bulk.

Recent work by Everest and Wallwork (*Journ. Soc. Dyers and Col.*, 1934, p. 40), however, would seem to indicate that, by the use of naphthols dispersed in soap solutions, or other dispersing agents, Azoic colours, eventually, will be applied successfully to the printing of woollen fabrics. It may be stated here that a dispersion of β-naphthol has been in constant use for twenty-five or more years in a well-known English printworks for the printing of Basic and Chrome colours in conjunction with Azoic red and claret blotches on cotton ; but, so far as the writer knows, the idea was never exploited on wool.

Practically all colouring matters belonging to the Acid, Basic, Mordant, Direct-dyeing, and Indigosol groups, and all Vat dyestuffs printed by the Rongalite-potash process, are suitable for wool printing.

From the many hundreds of colours thus available, comprising every shade of every colour in the spectrum and of diverse properties, it is easily possible to select complete ranges which satisfy most demands for brightness and fastness. Extreme fastness, though a most desirable quality in an expensive fabric like wool, does not, curiously enough, receive the same attention in wool printing as in cotton printing. To some extent it is not necessary, since printed woollen goods are never subjected to the somewhat drastic laundry treatment usually meted out to cotton goods—nor would the fabric itself stand such treatment. Then again, brilliant colours of reasonable fastness to light and careful washing are more attractive to the public than faster colours of quieter hue and, as they are simpler and cheaper to print, they satisfy both producer and consumer.

At the same time, the production of really fast colours, of considerable brightness, presents but little difficulty, and in many cases they must perforce be used for the printing of mixed fabrics of cotton and wool.

In the following description of the application of the numerous colours used in wool printing it is only possible to deal with a few examples of each group. These examples are typical of their respective groups or series, and other members of the groups may be applied by the same appropriate formulæ. For full ranges of suitable colours reference should be made to the Colour Index, published by the Society of Dyers and Colourists, or, more easily, to the manufacturers themselves.

(a) Acid Colours.

The Acid colours are more widely used than any other class of dyestuff for the printing of woollen fabrics. They are distinguished by their ease of application (fixing on the wool fibre without the aid of a mordant in most cases), their even printing qualities, and the unsurpassed brilliancy of the shades they yield. In fastness, the Acid colours vary between very wide limits: some are fast to light and loose to washing; others are loose to light and fast to washing; and others again are very fast to light and quite good to washing. By careful selection it is possible to get together a long range of Acid colours possessing very good fastness to light and satisfactory fastness to washing, rubbing, and running (bleeding) in the wet state. If a woollen print satisfies the latter conditions when washed at about 120°–140° F., it is considered to be of good quality.

Amongst the many groups of Acid colours on the market, dyestuffs suitable for any purpose of wool printing may be chosen from the following:—

Kiton Colours (S.C.I.B.).
Lissamine Colours
Naphthalene ,, (I.C.I.).
Disulphine ,,
Erio ,, (Geigy).
Tartrazine O.
Patent Blue — Fairly fast.
Naphthol Black B. (I.G.).
Brilliant Indocyanines
Milling Colours in general
Numerous Acid Scarlets, Reds, Yellows, Blues, Violets, Oranges, etc., of all makers.

Palatine Colours (I.G.).
Polar Colours (Geigy).
Coomassie Colours (I.C.I.). — Good general fastness.
Kiton Fast ,, (S.C.I.B.).

Alizarin Cyanines
,, Saphirols
,, Irisols
Acid Alizarin Colours (I.G.).
Anthranol ,,
Supramine ,, — Very good to light and washing.
Supranol ,,
Palatine Fast ,,
Solway ,, (I.C.I.).
Omega ,, (Sandoz).
Neolan ,, (S.C.I.B.).

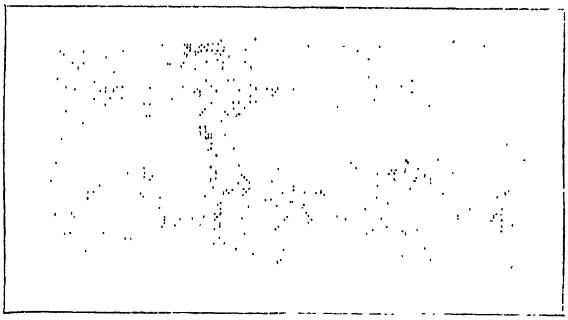
The Palatine Fast and Neolan colours are of exceptional interest on account of their excellent all-round fastness and their adaptability to both direct-printed and discharge styles.

Direct Printing.—Printing colours for wool are always thickened with easily soluble materials which wash out of the cloth readily in cold or slightly warm water. For this purpose Senegal, tragacanth and British gums are most generally used. Starch may be employed for fine outline and stipple engraving, but for ordinary object printing and for blotches it is unsuitable, because it requires a fairly long treatment in hot water or soap for its complete removal from the fibre, and if not removed it imparts an undesirable harsh feel to the cloth.

The natural affinity of wool for Acid dyestuffs is increased in the presence of organic acids or acid salts, and better fixation of the colouring matter is obtained when these form part of the printing pastes than when a simple thickened solution is printed.

The printing pastes consist essentially of dyestuff, thickening, and various acid assistants, *e.g.* acetic, formic, glycollic, oxalic, and tartaric acids, or oxalate or tartrate of ammonia. Glycerine, Fibrit D., Glyecine A., Resorcin, and Dissolving Salt B. find occasional use as solvents, and an addition of sodium chlorate is necessary in the case of Acid blacks, etc., where the reducing action of the fibre is to be counteracted, especially on unchlorinated material.

The great majority of Acid colours is, however, printed according to the simple methods illustrated in the following examples:—

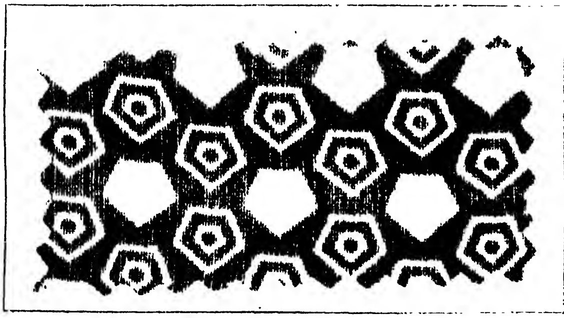


Kiton Fast Yellow R.N.: 30 grms. per Kilo. (S.C.I.B.).

YELLOW.

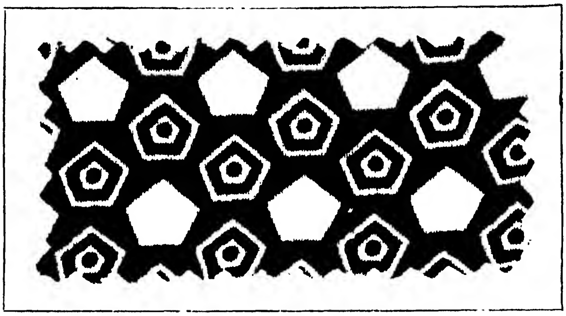
30	grms.	Kiton fast yellow R.N.
50	,,	glycerine.
320	,,	water.
Dissolve and		add to—
500	grms.	gum Senegal thickening.
50	c.c.	acetic acid 40 per cent.
50	c.c.	tartaric acid 50 per cent. solution.
1000	grms.	

The same recipe is also suitable for other colours of the same series, *e.g.* :—



Kiton Fast Orange 2 R.: 30 grms. per Kilo. (S.C.I.B.).

For less readily soluble colours a slightly different procedure is preferable, thus:—



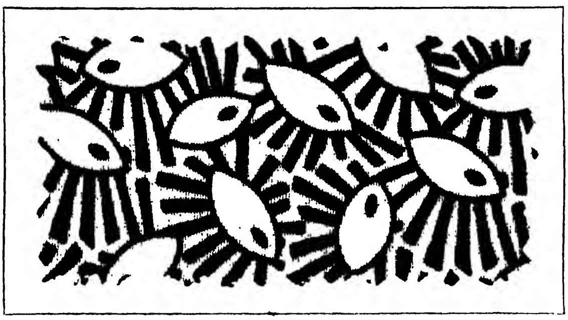
Kiton Fast Red B.L.: 30 grms. per Kilo. (S.C.I.B.).

RED.

30 grms. Kiton fast red B.L.
50 „ glycerine.
280 „ water.
Dissolve and add—
590 grms. Senegal or British gum thickening.
Warm together until completely dissolved, then add—
50 c.c. tartaric acid 50 per cent. solution.

1000 grms.

Easily fixed Acid colours of the ordinary types are merely printed with acetic acid or tartrate of ammonia, though the foregoing recipes are equally applicable to them.



Benzyl Fast Blue 3 G.L. dble. conc. for printing: 30 grms. per Kilo. (S.C.I.B.).

DARK BLUE.

30 grms. Benzyl fast blue 3 G.L. dble. conc. for printing.
50 „ glycerine.
300 „ water.
570 „ Senegal thickening.
50 c.c. tartrate of ammonia 32° Tw.

1000 grms.

After printing the goods are dried at a moderate temperature, steamed for 1 hour in moist steam, and finally well washed in running water and dried. The steaming is preferably carried out in a cottage steamer and without pressure.

Other recipes which yield excellent results with Acid colours are tabulated below.

ACID COLOUR RECIPES.

	I.	II.	III.	IV.
	grms.	grms.	grms.	grms.
Colouring matter	60	30	15	30
Glycerine	50	40	30	40
Glyecine A.	50	40	30	40
Resorcin	..	25	..	..
Water	280	290	300	270
British gum-tragacanth paste	..	500	..	..
Dissolve and add—				
British gum-tragacanth paste	500	..	500	500
Dissolving salt B.	..	..	30	..
Oxalate or tartrate of ammonia	30	30	20	20
Glycollic acid	30	30	..	..
Acetic acid 50 per cent.	..	..	..	100
Make up to	1000 grms. each.			

Reducing pastes for colours made up according to these recipes are prepared from the same ingredients (without dyestuff) in smaller proportions. It is not advisable, however, to reduce the glycerine, resorcin, and Glyecine A. to less than half the above quantities per kilo. nor the rest of the ingredients to less than one third.

Recipe I. is suitable for very dark shades of all colours. When used for Acid blacks, an addition of 10 grms. sodium chlorate per kilo. is necessary.

Recipe II. is adapted to ordinary Acid colours and many Anthranol, Acid alizarin, Supramine, Supranol, and Brilliant indocyanine dyes. In dissolving Anthranol violet 4 B.F., Anthranol blue G., and Alizarin pure blues F.F.B. and N.A. it is of advantage to beat up the dyestuff with 5–10 c.c. ammonia 25 per cent. and a little water before adding the other solvents and dissolving as described.

Recipe III. is used only for Supranol brilliant red 3 B.

Recipe IV. is chiefly employed for Alkali fast greens B.B.F. and 10 G., and for Supramine greens G. and B.L. The last two must be printed without ammonium oxalate.

The Acid colours include in their numerous groups practically every shade of colour required in printing, but where particular tones of colour are not easily matched by available dyestuffs they may readily be obtained from mixtures. Even blacks may be produced from mixtures of very dark blues with a small proportion of orange or reddish-yellow; they are, however, better obtained from one of the many Acid blacks on the market.

ACID BLACK.

60	grms.	Naphthylamine black 4 B.K. (I.G.).
50	,,	glycerine.
50	,,	Glyecine A.
260	,,	water.

Dissolve and add to—

500	grms.	British gum-tragacanth paste.
30	,,	oxalate of ammonia.
30	,,	glycollic acid.
20	,,	sodium chlorate 1 : 2.
1000		

Print, steam, and wash as already described.

Most of the Acid dyestuffs in current use may be applied by one or other of the foregoing formulæ or such modifications of them as may be required to conform with special conditions. For example, in the case of mixtures of dyestuffs, regard must be had to the solubility of the components. Some dyestuffs are precipitated by free acids and others by salts—oxalates, tartrates, etc.—so that, in such instances, they are unsuitable for mixing together; in short, only dyestuffs of similar solubilities or capable of being printed by alternative methods are adapted for the preparation of compound colours. There is, however, no dearth of them.

For block printing sulphate of alumina, tungstate of soda, and stannic chloride are employed to retard the fixation; they act by converting the colouring matter into an extremely fine precipitate, which is fixed in steaming. Very insoluble Acid colours require to be applied in neutral solutions, otherwise they both work badly and give specky prints. In such cases they are mixed with ammonium oxalate, which splits up in steaming, and supplies the acidity necessary to the full development of the colour on the fibre. Small amounts of ammonia are also frequently added to sparingly soluble dyestuffs, and they usually improve the levelling of the colour.

(*b*) NEOLAN AND PALATINE FAST COLOURS.

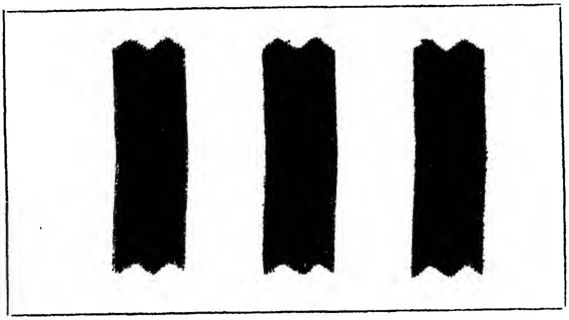
The members of these two groups of dyestuffs may be regarded as direct dyeing acid mordant colours inasmuch as, from a strongly acid bath, they dye wool with a chromium lake of the colouring matter, without either a previous mordanting of the material or a subsequent treatment with bichromate of potash (after-chroming). They contain chromium in the colour molecule, being chromium compounds of *o*-oxyazo dyes of a special type, and they differ fundamentally from all previous azo dyestuffs containing chromium salt-forming groups.

Whilst in dyeing the Neolan and Palatine Fast colours may be applied without any treatment whatsoever with chromium salts, it is necessary in printing to add chromium acetate to the printing paste in order to obtain the maximum fixation under the less acid conditions of steaming.

Though the shades produced by these dyestuffs lack the extreme brilliancy of many of those obtained from the ordinary Acid colours, they possess, on the other hand, the great advantage of being extraordinarily fast to light and washing, and are, at the same time, of considerable brightness and beauty and, when dyed, are easily dischargeable in white and colours with hydrosulphites. These qualities invest the Neolan and Palatine Fast colours with exceptional value and importance for the production of high-class woollen goods in direct-printed and discharge styles, because they afford a simple

means of obtaining colours which combine purity of shade and good all-round fastness in a degree not hitherto associated with Acid dyestuffs.

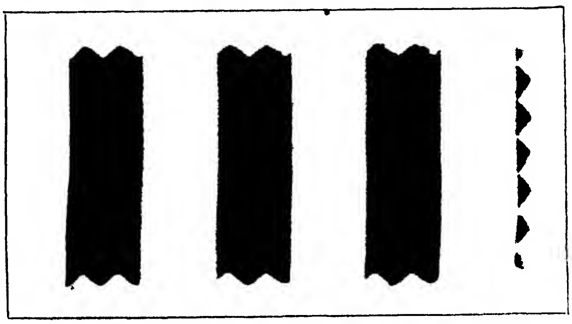
The *Neolan Colours* are printed by two recipes according to their solubility properties and depth of shade.



Neolan Yellow G.R.: 30 grms. per Kilo. (S.C.I.B.).

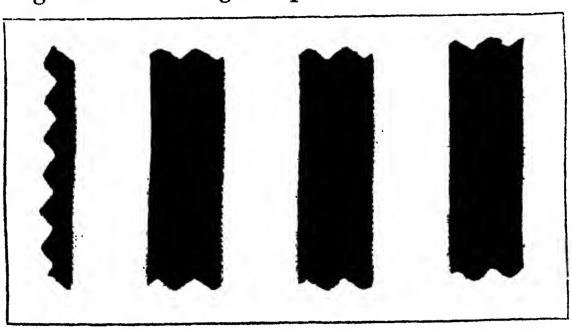
I. Yellow.

10– 30	grms.	Neolan yellow G.R.
370–310	,,	water. Dissolve at the boil and add—
550	,,	British gum thickening.
50	,,	glycerine. Cool and add—
20– 60	c.c.	chromium acetate 32° Tw.
1000	grms.	



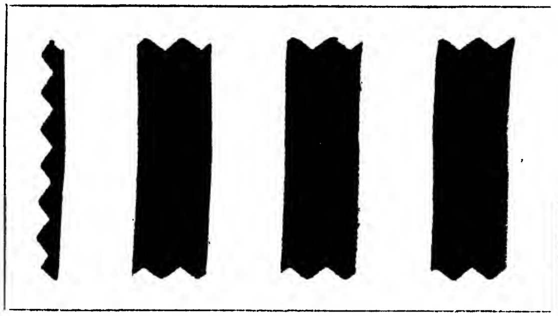
Neolan Pink B.A.: 30 grms. per Kilo. (S.C.I.B.).

Neolan pink B.A. and the following Neolan green B.L. conc. are made up according to the recipe above, which is suitable for all the more soluble colours containing from 10 to 30 grms. per kilo.



Neolan Green B.L. conc.: 30 grms. per Kilo. (S.C.I.B.).

II. A different method of dissolving the dyestuff is adopted in the case of all dark shades containing 30 to 60 grms. of dyestuff per kilo. of printing colour, for Neolan blacks and for all the less soluble Neolan colours. It may be used equally well for the whole of the Neolan group if desired. Two examples of this method are given below.



Neolan Brown G.R.: 30 grms. per Kilo. (S.C.I.B.).

BROWN.

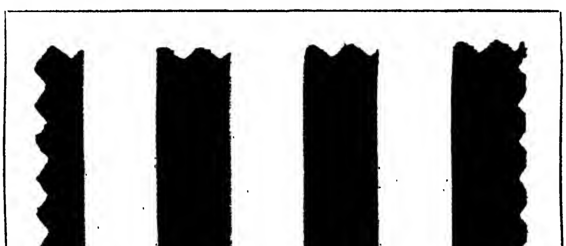
30– 60	grms.	Neolan brown G.R.
270–270	,,	dry British gum.

Mix together in the dry state and then beat up into a smooth paste with—

590–540	c.c.	cold water.

Heat until completely dissolved, cool, and add—

50– 50	c.c.	glycerine.
60– 80	,,	chromium acetate 32° Tw.
1000	grms.	



Neolan Navy Blue 2 R.L. conc.: 50 grms. per Kilo. (S.C.I.B.).

After printing, the goods are dried at a moderate temperature, steamed in a cottage steamer for 1 hour with moist steam without pressure, washed in running water until all traces of thickening and loosely adhering colour are removed, and finally dried.

The patterns illustrated here have been printed on chlorinated cloth.

The *Palatine Fast Colours*, which are analogous but not identical with the Neolan colours, are best printed in a fairly acid medium. Colours prepared on the lines of the recipe recommended by the makers (I.G. Farbenindustrie A.G.) give a better yield and brighter shades than less acid compositions.

EXAMPLE.

15– 60	grms.	Palatine Fast dyestuff.
30– 50	,,	glycerine.
30– 50	,,	Fibrit D. (or Glyecine A.).
345–190	,,	water.

Dissolve at the boil and mix with—

500–500	grms.	British gum-tragacanth paste.

Cool and add—

30– 50	,,	formic acid 85 per cent.
50–100	,,	chromium acetate 32° Tw.
1000		

REDUCING PASTE.

500	grms.	British gum-tragacanth paste.
410	,,	water.
20	,,	glycerine.
20	,,	formic acid 85 per cent.
20	,,	Fibrit D.
30	,,	chromium acetate 32° Tw.
1000		

BRITISH GUM-TRAGACANTH PASTE.

400	grms.	British gum dry.
400	,,	water.
200	,,	tragacanth mucilage 6 per cent.
1000		

Boil and cool.

Considerations of space preclude the inclusion of patterns of Palatine Fast colours here, but examples of their application to silk printing will be found in the following section.

The Neolan (S.C.I.B.) and Palatine Fast (I.G.) ranges both comprise a full scale of colours, both bright and quiet in tone, and thus render possible, by simple straightforward printing, the easy production of any type of multi-colour pattern in colours that are of consistent fastness throughout.

(c) BASIC COLOURS.

The employment of Basic colours on wool is very limited, owing to the fact that they are much looser to light than on cotton, or than the Acid colours. They are usually printed with acetic or other organic acid, and sometimes tannic acid is added for their better fixation.

PRINTING PASTE.	I.	II.
Basic dyestuff	25	25
Acetic acid 9° Tw.	100	100
Water	210	160
Tartaric acid	20	20
British gum	150	150
Gum tragacanth 6 per cent.	495	495
Boil, cool, and add—		
Acetic acid-tannin sol. 50 per cent.	..	50
	1000	1000

These two recipes are suitable for all Basic colours.

(*d*) Eosines.

The following formulæ are all suitable for the printing of Eosines :—

	I.	II.	III.	IV.
Colouring matter	45	10	10	10
Water	380	280	100	100
Gum Senegal 50 per cent.	275	700	730	730
British gum	200	..	..	..
Acetic acid	100	..	..	..
Phosphate of soda	..	..	40	..
Acetate of soda	..	..	..	40
Soda-ash	..	10	..	..
Stannous chloride	..	..	20	20
Water	..	..	100	100
	1000	1000	1000	1000

The presence of stannous chloride produces yellower shades and acts favourably with regard to the bleeding of the colours. All brands of Eosine, Rose Bengale, Erythrosine, Phloxine, Uranine, etc., are applicable by any of the above four recipes. After printing, steam, wash, and dry.

(*e*) Direct Colours.

The application of the Diamine colours will sufficiently illustrate the possibilities of the Direct colours in wool printing.

They are distinguished by their fastness to washing, and even to milling, by their good levelling properties, and by the sharpness of the impression they give of the engraved pattern. The Diamine colours (and other Direct dyestuffs) are printed with an addition of acetic acid, according to the following recipes. After printing, they are steamed, washed, and dried in the manner usual for wool, and they can therefore be employed in combination with any other wool colour :—

Direct Colours for Wool Printing.

40–60	grms.	Direct colour.
300	,,	water.
300	,,	gum Senegal thickening 50 per cent.
200	,,	British gum. Boil, cool, and add—
90	,,	acetic acid 12° Tw.
70–50	,,	water.
1000		

Suitable for Diamine blues 2 B., 3 B., and Diamine sky blue, Diamine scarlets B. and 3 B., all of which are most useful for printing heavy patterns for dress goods. Other Direct colours (Diamines included) are applied in a similar way, and various compound shades can be readily obtained by mixing.

(*f*) Mordant Colours.

The Mordant colours are generally assumed to embody the acme of fastness attainable in wool printing and dyeing. This postulate, however, calls for some qualification, since many Mordant colours leave much to be desired in respect of fastness, especially as regards light, and because, also, the introduction of the Neolan and Palatine Fast dyestuffs has made it possible to produce, *without Mordants if need be*, a full range of colours which cede nothing in fastness to the best of the Mordant dyestuffs. Moreover, the Vat colours and their derivatives, the Indigosols, are also applicable to wool printing, and although employed only to a limited extent at present, they provide a potential source of an enormous range of very fast shades, including the most permanent colours known. Thus, it will be seen that, classified according to fastness, the Mordant colours form part of an important group, rather than a group apart.

The Mordant colours are employed chiefly in the printing of the better-class dress goods in which fastness to light, washing, and perspiration are of prime importance, and also for decorative and furnishing fabrics, flags, bunting, etc., which are required to resist the action of light and other destructive influences. Of late years, fastness to sea-water and sea-air has also become a question of importance.

In addition to the ordinary Chrome Mordant colours, so largely used in cotton printing, there is available for wool printing a further wide and comprehensive range of Acid Mordant dyestuffs which may be printed equally well on chlorinated or unchlorinated cloth, either with or without mordant. If printed without mordant, in the manner of ordinary Acid colours, they give shades which are fast to light, but not otherwise notable ; on the other hand, if printed along with chromium mordants their fastness to washing is remarkably increased.

The following list contains a few of the better known of the many groups of Mordant dyestuffs used in wool printing :—

*Alizarin	all brands	(I.C.I.).	Anthracene Chrome	colours	(I.G.).
* ,,	orange	(,,).	Acid anthracene	,,	(,,).
* ,,	bordeaux	(,,).	Acid alizarin	,,	(,,).
* ,,	yellows	(,,).	Acid chrome	,,	(,,).
* ,,	blue	(,,).	Salicin	,,	(,,).
Eriochrome	colours	(Geigy).	Chrome fast	,,	(S.C.I.B.).
Metachrome	,,	(Br.).	Monochrome	,,	(L.B.H.).
Solochrome	,,	(I.C.I.).	Erachrome	,,	(I.C.I.).
*Modern and Chrome	colours	(D. & H.).	*Ultra (chrome)	,,	(Sandoz).

The groups marked * are ordinary Mordant dyestuffs and applicable to either wool or cotton.

Other Mordant colours may equally well be employed in the printing of all types of woollen fabrics ; in fact it may be taken that all synthetic and vegetable Mordant dyestuffs, capable of working satisfactorily in an acid medium, are suitable for the purposes of wool printing.

The preparation of printing colours for wool differs little from that for cotton, except in the matter of acidity. The best results are obtained in the presence of the stronger organic acids—oxalic, tartaric, glycollic, or formic acid—though acetic acid alone is frequently used on economic grounds. As mordants, only the salts of aluminium and chromium come into consideration, viz. acetate, formate, or fluoride of chromium, and acetate or sulphate of aluminium.

The following examples illustrate the general methods of making up Mordant printing colours :—

MORDANT PRINTING COLOURS.

	I.	II.	III.
	grms.	grms.	grms.
Mordant dyestuff (powder)	30	30	..
„ „ 20 per cent. paste	..	..	150
Glycerine	30	30	30
Water	150	150	..
British gum-tragacanth paste	580	580	580
Oxalic acid	25	25	20
Formic acid 90 per cent.	..	..	25
Chromium acetate 32° Tw.	120	..	..
Chromium fluoride dry	..	30	..
Aluminium sulphate dry	..	..	50
Water	65	155	145
	1000 grms. each.		

Recipes I. and II. are suitable for all Mordant dyestuffs ; recipe III. is used for all brands of Alizarin, Alizarin orange, Alizarin bordeaux, and Alizarin cyclamin—whether ordinary or acid colours.

The colouring matter is dissolved, by heat, in the glycerine, water, and thickening, and cooled ; the acid, dissolved in a portion of the water, is then added, and the printing colour completed by addition of the appropriate mordant.

IV. ACID ALIZARIN RED.

30 grms. Alizarin red S.A. powder (I.C.I.).
250 „ boiling water.
500 „ tragacanth mucilage 65 : 1000.

Boil, cool, and add—

50 grms. aluminium sulphate.
25 „ oxalic acid.
130 „ water.
15 „ Lizarol D. (or similar product).

1000

V. ALIZARIN BLUE.

40 grms. Alizarin blue S. (I.C.I.).
100 „ water.
530 „ tragacanth mucilage 65 : 1000.

Dissolve in the cold and add—

30 grms. tartaric acid.
200 „ water.
100 „ chromium acetate 32° Tw.

1000

Other gum thickenings, *e.g.* Senegal, Arabic, British gum, and mixtures of the last-named with tragacanth, may be used if desired ; but starch thick-

enings are employed only for outlines and small objects like spots, sprigs, etc., as starch is difficult to remove from the fibre under the usual conditions obtaining in the after-treatment of wool prints.

Any Mordant printing colour may be "toned" or modified in shade by the addition of ordinary acid azo dyestuffs such as Patent blue, Formyl violet S. 4 B., Kiton fast orange 2 R., Supramine red G.G., Guinea green B., etc.

After printing, the goods are steamed in a cottage steamer for 1–2 hours in damp steam at 2½–3 lb. pressure, and then washed and dried as usual. If desired, a light soaping at 120° F. may be given before the final wash.

Mordant colours in general give somewhat quieter shades than other classes of dyestuffs and are used chiefly for the fastest work and for dark heavy blotch shades in multicolour patterns. Brilliance of shade is not always a concomitant of fastness and, consequently, it frequently happens that, where a high degree of fastness is demanded, some concession in brightness must be made. (See also "Silk Printing.")

(*g*) Vat Colours.

Although the Vat dyestuffs are well adapted to the printing of wool, they are employed only in rare cases where, for some particular purpose, exceptional fastness to soaping is required.

The nature of the wool fibre precludes the use of caustic alkalies in the printing colours, so that only such Vat dyestuffs as can be applied with potassium or sodium carbonate are available. Of these there is no lack, as practically all modern Vat colours, of any interest, are applicable by the Rongalite-potash process. An increase in the glycerine content tends to the preservation of the fibre during steaming, though, under ordinary conditions, little danger need be apprehended in this direction. At the same time it is advisable to minimise the risk of damage by reducing the alkali content of the printing pastes to as low a point as is consistent with the proper fixation of the colouring matter. In many instances, however, the ordinary Rongalite-potash printing pastes, used for cotton, may equally well be printed on wool without fear of injury to the fibre.

The Vat colours may be printed in the unreduced state by the ordinary Rongalite-potash process or by the pre-reduction method which, as a rule, gives superior results. The following general recipe, based on the latter method, has worked satisfactorily in practice :—

Vat Printing Colour for Wool.

{100–150	grms.	Vat dyestuff double paste fine.
{30	,,	glycerine.
670	,,	potash thickening (below).
30	,,	sodium hydrosulphite conc. ($Na_2S_2O_4$).

Heat to 140° F. until completely reduced, then add—

{40–60	grms.	Formosul or Rongalite C.
{40–60	,,	water.
90	,,	British gum thickening (or water).
1000		

Potash Thickening.

300	grms.	water.
220	,,	British gum powder.
20	,,	Dissolving salt B.
80	,,	potassium carbonate.
50	,,	glycerine.
670		

Boil and cool.

Reducing Paste for Lighter Shades.

670	grms.	potash thickening (above).
1330	,,	British gum thickening.
2000		

The foregoing formulæ are suitable for all Indigoid dyestuffs in the Durindone and Ciba ranges, and also for the majority of dyestuffs in the Indanthrene, Caledon, Algole, Anthra, and other series of Anthraquinone colours.

The printed goods are dried carefully in hot air, steamed for 5 minutes in the rapid ager in damp air-free steam at 214°–216° F., washed thoroughly in cold water, soaped at 120° F. with the addition of 2 grms. of sodium perborate per litre, washed, soured in sulphuric acid, $\frac{1}{4}$–$\frac{1}{2}$° Tw., washed again and dried.

(*h*) Indigosols in Wool Printing.

The Indigosols lend themselves admirably to the printing of wool when applied by suitable methods, and being printed in neutral or slightly acid media, they afford a means of obtaining full, bright, and extremely fast Vat colours without the slightest risk of injury to the woollen fibre.

The methods employed in cotton printing are less satisfactory when applied to wool. The chlorate steaming processes yield full, bright shades which, unfortunately, suffer from the disadvantage of not being very fast to rubbing; the nitrite and bichromate processes also give good development of the colours, but stain the white ground so badly as to be quite inadmissible in practice.

Recently, however, the I.G. Farbenindustrie A.G. has worked out two improved processes which not only overcome the foregoing drawbacks and yield deep wool prints of excellent fastness to rubbing, light, washing, sea-water, and perspiration, but are also simple and reliable in operation. They are known as the *lead chromate* and *sodium chlorate* processes, respectively.

The Lead Chromate Process.—By this process the Indigosol dyestuff, along with lead chromate and ammonium sulphocyanide or Developer D., is printed on chlorinated wool and, after a short steaming, is developed by a passage through a hot bath of mixed hydrochloric and oxalic acids, in which the parent vat colour of the Indigosol is regenerated by the oxidising action of the chromic acid set free from the lead chromate.

The printing colours are prepared according to the usual procedure for Indigosols, except in the case of Indigosol brown I.R.R.D. This colour, after mixing into a paste with glycerine, is heated and then re-precipitated in a finely divided state by stirring into it a cold aqueous solution of the prescribed quantity of ammonium sulphocyanide; the suspension so obtained is stirred into the thickening and the urea added and dissolved.

INDIGOSOL PRINTING COLOURS: LEAD CHROMATE PROCESS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Indigosol Yellow H.C.G.	40	..	..	..	..	..	..	..	..	..	..	..
,, Golden Yellow I.G.K.	..	30	..	..	..	..	..	..	..	..	..	..
,, ,, I.R.K.	..	..	50	..	..	..	..	..	..	..	..	..
,, Orange H.R.	..	..	..	60	..	..	..	..	..	..	..	..
,, Scarlet H.B.	..	..	..	..	60	..	..	..	..	..	..	..
,, ,, I.B.	..	..	..	..	..	60	..	..	..	..	..	..
,, Pink I.R. extra	..	..	..	..	..	..	40	..	..	..	..	..
,, Red H.R.	..	..	..	..	..	..	..	60	..	..	..	..
,, Brilliant Pink I. 3 B.	..	..	..	..	..	..	..	..	60	..	..	..
,, Red Violet I.R.H.	..	..	..	..	..	..	..	..	..	50	..	..
,, Printing Purple I.R.	..	..	..	..	..	..	..	..	..	..	50	..
,, Violet A.Z.B.	..	..	..	..	..	..	..	..	..	..	..	50
Glycerine	80	80	80	80	80	100	80	100	80	80	100	100
Indigosol Developer G.A.	..	30	30	30	30	..	30	..	30	30	..	..
,, ,, D.	30	..	..	..	..	..	..	..	..	30	..	..
Water	300	310	290	250	240	250	260	220	240	190	260	260
Stock thickening	550	550	550	550	550	550	550	550	550	550	550	550
Ammonium sulphocyanide	..	..	..	30	40	40	40	40	40	40	40	40
Lead chromate paste 60 per cent.	..	..	..	..	..	..	..	30	..	30	..	..
	1000 grms. each.											

	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.
Indigosol Printing Violet I.B.B.F.	40	..	..	..	..	..	..	..	..	..	..
,, Printing Blue I.B.	..	50	..	..	..	..	..	..	..	..	..
,, H.B.	..	..	40	..	..	..	..	..	..	..	..
,, O. 4 B.	..	..	..	40	..	..	..	..	..	..	..
,, O.R.	..	..	..	..	60	..	..	..	..	..	..
,, A.Z.G.	..	..	..	..	..	40	..	..	..	..	..
,, Printing Blue I.G.G.	..	..	..	..	..	..	30	..	..	..	..
,, O.6 B.	..	..	..	..	..	..	..	40	..	..	..
,, Green A.B.	..	..	..	..	..	..	..	..	45		
,, Brown I.R.R.D.	..	..	..	..	..	..	..	..	..	40	..
,, Printing Black I.B.	..	..	..	..	..	..	..	..	..	..	80
Glycerine	100	100	80	100	100	100	100	100	80	100	100
Indigosol Developer G.A.	..	..	30	..	..	..	..	..	30	..	..
,, ,, D.	..	..	..	..	..	..	..	..	30	..	..
Water	270	260	210	270	250	270	280	270	265	240	230
Stock thickening	550	550	550	550	550	550	550	550	550	550	550
Ammonium sulphocyanide	40	40	60	40	40	40	40	40	..	40	40
Lead chromate paste 60 per cent.	..	..	30	..	..	..	..	..	..	..	..
Urea	..	..	..	..	..	..	..	..	..	30	..
	1000 grms. each.										

STOCK THICKENING.

$\begin{cases}\text{220 grms. lead chromate 60 per cent. paste.}\\ \text{ 80 ,, Igepon T. (1 : 10).}\end{cases}$

Mix and add—

300	grms.	tragacanth mucilage 60 : 1000.
320–290	,,	British gum 1 : 1.
60– 90	,,	sodium acetate.
20	,,	turpentine.
1000		

THICKENING FOR REDUCTIONS.

{ 80	grms.	lead chromate paste 60 per cent.
{ 50	,,	Igepon T. (1 : 10).
80	,,	glycerine.
460	,,	British gum-tragacanth thickening.
50	,,	sodium acetate.
30– 50	,,	ammonium sulphocyanide.
230–210	,,	water.
20	,,	turpentine.
1000		

Igepon T. is a powerful dispersing and levelling agent. Sodium acetate is added to prevent premature development of the Indigosols during steaming —development which may easily arise if the wool has retained (as sometimes happens) considerable quantities of mineral acid from the chlorinating or bleaching operations.

LEAD CHROMATE PASTE, 60 PER CENT.

(A) { 2274 grms. lead acetate.
10 litres water.

(B) { 885 grms. sodium bichromate.
10 litres water.

Add (A) to (B), wash four times by decantation, and filter the precipitate to a paste containing 60 per cent. solids.

Print the colours tabulated above on chlorinated material; dry and steam with moist steam at 214° F. for 10 minutes in the rapid ager; develop by passing the goods in the open width through a *hot* acid bath containing—

{ 25 c.c. hydrochloric acid 36° Tw.
3–5 grms. oxalic acid.
1000 c.c. water.

Duration of acid passage, 40–50 seconds. Temperature, 190°–205° F. On leaving the developing tank the goods are lightly washed, passed through a hot bath (120°–170° F.) of sodium bisulphite (15 c.c. $NaHSO_3$ 72° Tw. per litre) for ½–1 minute, washed thoroughly and soaped for 5 minutes with addition of 2 grms. of Igepon T. per litre at 140° F., washed again and dried. The acid development is best carried out in roller tanks of wood or acid-resisting material.

THE SODIUM CHLORATE PROCESS.—This process differs from the preceding in that the printing colours contain only Indigosol solution, an acid-yielding agent, an oxygen carrier (ammonium vanadate), and thickening, the oxidising agent—sodium chlorate—being contained in the acid developing bath.

In preparing the printing colours for this process, the Indigosol dyestuff is first dissolved in hot water, glycerine, and other solvents, and ammonium vanadate added according to the quantities indicated below; it is then incorporated with the thickening and the colour completed by adding the rest of the components.

Indigosol brown I.R.R.D. is again an exception and must be heated with Dissolving salt B., glycerine, and Fibrit D. until a perfectly smooth paste is obtained. The dyestuff is then converted into an extremely fine suspension by the successive additions of the stated amounts of cold water, ammonium vanadate solution (1 : 100), and ammonium sulphocyanide, and, in that condition, is stirred into the thickening, the urea being added last.

INDIGOSOL PRINTING COLOURS: SODIUM CHLORATE PROCESS.

	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.	12.
Indigosol Yellow H.C.G.	40	..	..	..	..	..	..	..	..	..	..	..
„ Golden Yellow I.G.K.	..	30	..	..	..	..	..	..	..	..	..	..
„ „ I.R.K.	..	..	50	..	..	..	..	..	..	..	..	..
„ Orange H.R.	..	..	..	60	..	..	..	..	..	..	..	..
„ Scarlet H.B.	..	..	..	..	60	..	..	..	..	..	..	..
„ „ I.B.	..	..	..	..	..	60	..	..	..	..	..	..
„ Pink I.R. extra	..	..	..	..	..	..	40	..	..	..	..	..
„ Red H.R.	..	..	..	..	..	..	..	60	..	..	..	..
„ Brilliant Pink I. 3 B.	..	..	..	..	..	..	..	..	60	..	..	..
„ Red Violet I.R.H.	..	..	..	..	..	..	..	..	..	50	..	..
„ Printing Purple I.R.	..	..	..	..	..	..	..	..	..	..	50	..
„ Violet A.Z.B.	..	..	..	..	..	..	..	..	..	..	..	50
Dissolving Salt B.	..	..	..	10	10	..	20	..	10	..	..	..
Igepon T.	..	..	5	5	..	..	..	..	..	..	..	..
Glycerine	80	80	80	80	80	80	80	100	80	80	100	100
Glyecine A.	30	30	50	50	50	50	50	..	40	50	..	..
Indigosol Developer G.A.	..	30	20	..	..	..	..	..	..	..	..	..
„ „ D.	40	40	40	..	..	..	..	..	..	30	..	..
Water	210	190	135	155	40	20	45	50	20	10	60	60
Ammonium vanadate 1 : 100	50	50	50	50	200	200	200	200	200	220	200	200
British gum thickening 1 : 1	550	550	550	550	520	550	525	550	550	520	550	550
Ammonium sulphocyanide	..	..	10	40	40	40	40	40	40	40	40	40
Ammonia 25 per cent.	..	..	10	..	..	..	..	..	..	..	..	..
	1000 grms. each.											

	13.	14.	15.	16.	17.	18.	19.	20.	21.	22.	23.
Indigosol Printing Violet I.B.B.F.	40	..	..	..	..	..	..	..	..	..	..
„ Printing Blue I.B.	..	50	..	..	..	..	..	..	..	..	..
„ H.B.	..	..	40	..	..	..	..	..	..	..	..
„ O. 4 B.	..	..	..	40	..	..	..	..	..	..	..
„ O.R.	..	..	..	..	60	..	..	..	..	..	..
„ A.Z.G.	..	..	..	..	..	40	..	..	..	..	..
„ Printing Blue I.G.G.	..	..	..	..	..	..	30	..	..	..	..
„ O. 6 B.	..	..	..	..	..	..	..	40	..	..	..
„ Green A.B.	..	..	..	..	..	..	..	..	45	..	..
„ Brown I.R.R.D.	..	..	..	..	..	..	..	..	..	40	..
„ Printing Black I.B.	..	..	..	..	..	..	..	..	..	..	80
Dissolving Salt B.	..	..	30	..	..	..	..	..	..	30	..
Glycerine	100	100	80	100	100	100	100	100	80	50	100
Glyecine A.	..	..	50	..	..	..	..	..	50	..	..
Indigosol Developer G.A.	..	..	..	..	..	..	..	..	30	..	..
„ „ D.	20	..	..	..	..	..	..	..	50	30	..
Fibrit D.	..	..	..	..	..	..	..	..	..	60	..
Water	50	60	10	70	50	220	130	70	45	10	30
Ammonium vanadate 1 : 100	200	200	225	200	200	50	150	200	150	200	200
British gum thickening 1 : 1	550	550	525	550	550	550	550	550	550	500	550
Ammonium sulphocyanide	40	40	40	40	40	40	40	40	..	40	40
Urea	..	..	..	..	..	..	..	..	..	40	..
	1000 grms. each.										

British gum may be replaced in any of the foregoing printing colours by tragacanth or other natural gums used in wool printing, or by mixtures of these with British gum.

For light shades reduced from the above recipes the following thickening is used :—

REDUCTION THICKENING.

550	grms.	British gum, or other thickening.
50	,,	glycerine.
50	,,	ammonium vanadate (1 : 100).
20– 40	,,	ammonium sulphocyanide or Developer D.
330–310	,,	water.
1000		

After printing on chlorinated cloth, the goods are steamed in the rapid ager for 10 minutes in damp steam, and then developed in the open width by a passage of 25–30 seconds through a hot bath of—

$$\left.\begin{array}{l}\text{25 c.c. sulphuric acid 168° Tw.}\\ \text{30 grms. sodium chlorate}\end{array}\right\}\text{per litre}$$

at 185°–205° F. They are then washed, treated in bisulphite of soda, soured, soaped, and washed as described for the Lead Chromate process.

The sodium chlorate process is equally suitable for padding plain shades on a mangle, for which purpose the quantity of thickening indicated for printing colours is reduced, care being taken, at the same time, not to reduce the vanadate of ammonia (1 : 100) below 50 c.c. per litre nor the sulphocyanide of ammonia below 20 grms. per litre, even for pale shades.

The lead chromate and sodium chlorate processes are applicable to all Indigosols except Indigosol O. and Indigosol green I.B.A., neither of which yields satisfactory results.

Block Printing on wool requires the colours to be specially prepared with a view to preventing their fixation on the fibre in the cold. Frequently, too, the cloth undergoes a special preparation in tin, for the purpose of obtaining brighter colours than are otherwise obtainable.

The preparation is effected as follows :—The cloth, chlorinated as already described, is first well washed and squeezed, and then passed through a bath containing—

$$\left\{\begin{array}{l}\text{200 litres Tin Liquor W.B.}\\ \text{400 ,, water.}\end{array}\right.$$

TIN LIQUOR W.B.

$\left\{\begin{array}{lll}12 & \text{kilos.} & \text{oxalic acid.}\\ 120 & ,, & \text{boiling water. Add, whilst stirring—}\end{array}\right.$

$\left\{\begin{array}{lll}12 & ,, & \text{stannate of soda.}\\ 120 & ,, & \text{water (boiling). And when the mixture is clear add—}\end{array}\right.$

10 ,, ammonia 25 per cent. Make up to 250 litres with water.

The goods pass through this bath in the open width, and on emerging excess of liquor is extracted by means of a pair of squeezing rollers ; they are then allowed to lie in pile for 3 hours, and finally hydro-extracted and dried to width on a stentering machine, without washing.

This special tin preparation has not merely the advantage of giving brighter colours, but it also reduces their tendency to run during the time that they lie in the wet state on the printing table.

In the printing of wool by block, it is advisable to commence with the outlines (if there are any), and to print these in colours thickened with British

gum and wheat starch. By proceeding in this manner, the possibility of the thinner and lighter colours running into each other, if not always prevented entirely, is reduced to a minimum. The spreading of a lighter shade into a dark blue, chocolate, or black outline is unnoticeable, whereas, if the reverse were to occur, the effect would be ruined.

The most important colours for block printing are those which level well during the steaming operation, and of these the following are amongst the best:—Brilliant cochineals 2 R. and 4 R., Amaranth, Ruby red A., Cyanol extra, Formyl violet S. 4 B., Naphthol black B., Auramine, Phosphine, Uranine, Tartrazine, Eosine, Croceine Orange C., Rose bengale, Erythrosine, Quinoline yellow, Palatine scarlet, Alkali blue, Flavazine and Sulphon-carmine C. Besides these, almost any wool colour suitable for machine printing may be employed for dark shades in block work.

The differences between the composition of block- and machine-printing colours relate mainly to the preparation of blotch colours; for floral and other light patterns, any of the printing colours used for roller printing are generally equally well adapted to block work, always provided that the repeats of the design show fully completed objects on the block.

The following typical recipes will serve as illustrations of the methods adopted in practice for the preparation of colours for block printing by hand.

Dark Blue Outline Colour.

45	grms.	Fast blue B.D.
725	,,	water.
80	,,	wheat starch.
150	,,	British gum.
1000		Boil and cool.

Chocolate outlines are produced from a mixture of Orchil extract with a little of the above blue, and are similarly thickened.

Black Blotch.

80	grms.	Naphthol black B.
400	,,	water.
426	,,	gum Labiche 60 per cent.
{ $2\frac{1}{2}$	,,	Acid green extra conc.
{ $1\frac{1}{2}$	,,	Tartrazine O.
{ 35	,,	water.
{ 15	,,	sulphuric acid 168° Tw.
{ 40	,,	water.
1000		

Navy Blue (Blotch).

220	grms.	Gallazine blue A. 15 per cent. (Durand and Huguenin).
220	,,	water.
45	,,	acetine.
7	,,	ammonia 25 per cent.
Boil, and add—		
{ 80	grms.	China clay.
{ 40	,,	water.
45	,,	British gum.
333	,,	tragacanth thickening 6 per cent.
10	,,	chlorate of soda.
1000		Cool.

VARIOUS BLOTCHES.

	BLUE.	ROSE.	GREEN.	MAROON.	RED.	CLARET.
	grms.	grms.	grms.	grms.	grms.	grms.
Cyanol extra	16	..	..	..	..	..
Rose bengale	..	25	..	..	..	..
Thioflavine T.	..	..	8	..	..	..
Brilliant green	..	..	2	0·5	..	..
Amaranth	..	..	..	42	..	55
Orange extra	..	..	..	7	..	3
Formyl violet S. 4 B.	..	..	..	0·5	..	0·5
Ruby red A.	..	..	..	..	40	..
Water	150	320	309	330	400	301·5
Gum Senegal 50 per cent.	660	600	600	600	500	500
Oxalic acid	..	..	..	10	..	..
Oxalate of ammonia	..	..	..	..	..	15
Tartaric acid	..	..	8	..	30	..
Acetic acid 12° Tw.	25	..	..	..	..	..
Tungstate of soda	..	..	8	10	30	..
Stannic chloride 142° Tw.	..	..	25	..	..	25
Bisulphite of soda 90° Tw.	..	..	40	..	..	..
Ammonia 25 per cent	10	..	..	..	..	..
Acetate of ammonia solution 25 per cent.	114	..	..	..	..	..
Glycerine	25	..	..	..	..	..
Acetate of soda	..	35	..	..	..	..
Stannous chloride	..	20	..	..	..	..
	1000 grms. each.					

In preparing the above colours, the colouring matter is first dissolved in a portion of the water, then added to the gum, and the whole warmed together. After cooling, the other ingredients, dissolved separately in the remaining water, are added to the gum colour paste, and, after well mixing and straining, the colour is ready for printing.

The above recipes may be employed for all members of the groups to which their respective colours belong.

Discharge Styles on Wool.—The production of discharge effects on wool is confined to grounds dyed with Acid dyestuffs, Direct or Substantive dyestuffs, Acid mordant colours, Metachrome colours and certain Acid, Direct and Chrome colours which can be dyed, in fast shades, by the Metachrome process.

The discharging agents employed are generally hydrosulphites of various brands, less generally stannous chloride or acetate, or potassium sulphite, and, very occasionally, mixtures of zinc powder with bisulphite of soda. Oxidation discharges are not used on wool.

Of the various classes of dyestuffs used for ground shades, the ordinary Acid azo dyestuffs are the most widely employed, combining as they do ease of application with brilliancy and moderate fastness. Acid dyestuffs yield colours of fair to excellent fastness to light but, with a few exceptions, of only moderate resistance to water, washing, and perspiration. Amongst the colours of superior fastness may be mentioned the Coomassie colours, which are good to light and washing; the Supramine and Supranol series—good to light; and the Neolan and Palatine Fast dyestuffs, which are excellent to light, washing, perspiration, etc.

The Direct dyestuffs, as a class, are less brilliant in shade but much faster to washing than the Acid colours. In respect of fastness to light, dyestuffs of Chlorazol Fast, Chlorantine Fast, and other Fast types are excellent; others vary considerably in their resistance to light.

Where a high standard of all-round fastness is demanded, recourse is had to the Neolan and Palatine Fast dyestuffs, the properties of which have been described already in the section on wool printing. In addition to these, however, many Metachrome dyestuffs, and others dyed by the Metachrome process, are very suitable for fast discharge styles, those mentioned in the list below being of very good to excellent fastness to water, sea-water, washing, and perspiration, and, generally, of good to excellent fastness to light.

The following list contains only a selection of the hundreds of dyestuffs dischargeable by hydrosulphites and also, in some cases, by tin salts :—

ACID COLOURS.

Metanil yellow Y.K.S.	(I.C.I.).	Milling orange G.	(I.G.).
Coomassie yellows O.S. and R.S.	(,,).	,, scarlet B.	(,,).
,, red P.G.S.	(,,).	,, red 6 B.A.	(,,).
,, navy blues	(,,).	Supranol orange G.S.	(,,).
,, green T.S.	(,,).	(T) Various Croceine scarlets	(,,).
,, brown G.S.	(,,).	Acid green G.B.	(,,).
(T) Croceine scarlet 3 B.S.	(,,).	Light green S.F.	(,,).
Sorbine reds G. and B.B.N.	(I.G.).	Wool discharge black Y.D.	(,,).
Wool discharge blue N.	(,,).	Palatine Fast dyestuffs	(,,).
,, blue S.L.	(,,).	(T) Flavazine S.	(,,).
Brilliant indocyanine G.	(,,).	(T) Various Ponceaux.	
Neolan dyestuffs	(S.C.I.B.).	(T) Azo wool violet 7 R.	(I.G.).
(T) Tartrazine	(I.G.).	(T) Victoria violet 4 B.S.	(,,).
(T) Orange II.		(T) ,, ,, R.L.	(,,).
(T) Azofuchsine 6 B.	(I.G.).	Erioviridine B.	(Geigy).
(T) Brilliant sulphonazurine R.	(,,).	Discharge blue	(,,).
(T) Sulphon acid greens B., 2 B.L.	(,,).	(T) Azo acid black 3 R.L. extra.	(I.G.).
Supramine yellow R.	(,,).	Naphthylamine black 4 B.L.	(,,).
,, brown R.	(,,).	Lanafuchsine S.G.	(,,).
Milling yellow O.	(,,).	(T) Discharge black B.F. extra.	(,,).

Colours prefixed by " T " are also dischargeable with tin salts.

DIRECT DYESTUFFS.

Chlorazol Fast yellow 5 G.K.S.	(I.C.I.).	Chlorazol sky blue F.F.S.	(I.C.I.).
,, ,, ,, 8 G.S.	(,,).	,, greens B.N.S., G.S.	(,,).
,, ,, orange G.S.	(,,).	,, brown M.S. (dev.)	(,,).
,, ,, pink B.K.S.	(,,).	,, black E.S.	(,,).
,, ,, red K.S.	(,,).	Chrysophenine G.S.	(,,).
,, ,, bordeaux 6 B.S.	(,,).	Chicago blue 6 B.	(I.G.).
,, ,, heliotropes B.K.S., 2 R.K.S.	(,,).	Diamine green G.	(,,).
Chlorantine group	(S.C.I.B.).	Benzo Fast group	(,,).
Chloramine ,,	(Sandoz).	Diamine ,,	(,,).
Diphenyl ,,	(Geigy).	Dianil ,,	(,,).

With very few exceptions the members of these several groups of dyestuffs are all readily dischargeable with hydrosulphites and tin salts.

METACHROME COLOURS AND COLOURS DYED BY THE METACHROME PROCESS.

Acid chrome yellows G.L., R.L. extra	(I.G.).	Chrome oranges G.R., L.R.	(I.G.).
Anthracene yellows B.N., C.	(,,).	Supranol orange G.S.	(,,).
Diamond flavine G.	(,,).	Anthracene acid red G.	(,,).
* Metachrome orange 3 R. dble.	(,,).	,, ,, reds * 3 B., 5 B.L.	(,,).
,, violet R.R.	(,,).	Cloth red G. extra	(,,).
,, blue B.A.	(,,).	Diamine fast red F.	(,,).
,, blue black B.B.X.	(,,).	Supranol red B.R.	(,,).
,, brilliant blue 8 R.L.	(,,).	Acid chrome red B.	(,,).
,, brown 6 G.	(,,).	* Chromoxane brilliant violet S.R.	(,,).
,, olives B., G.G.	(,,).	* Chromogene violet B.	(,,).
* Chromoxane azurol B.D.	(,,).	* Brilliant indocyanines G., 6 B.	(,,).
* ,, pure blue B.	(,,).	Anthracene chrome blue R.W.N.	(,,).

The dyestuffs marked * are less fast to light than the rest. Black and

numerous shades of green, olive, brown, etc., are obtained by mixing any of the foregoing Metachrome type of colours. Colours dyed by the Metachrome process are suitable only for hydrosulphite discharges, with which they give satisfactory whites.

Dyeing of Acid Colours.—The goods are entered into a lukewarm bath containing—

I. { 1–6 per cent. Acid dyestuff.
10 ,, ,, Glauber's salt.
4 ,, ,, sulphuric acid 168° Tw.

or

II. { 1–6 per cent. Acid dyestuff.
20 ,, ,, Glauber's salt.
5 ,, ,, acetic acid 12° Tw.

Raise the temperature gradually during ¾ hour to the boil and boil for 1 hour. If the bath is not exhausted, add a further 5 per cent. acetic acid or 2 per cent. sulphuric acid and, if necessary, 10 per cent. Glauber's salt. Wash and dry.

Neolan and Palatine Fast colours are dyed in stronger acid baths. The dye bath is set with—

{ 4–5 per cent. sulphuric acid 168° Tw.
10 ,, ,, Glauber's salt.
Water, a sufficiency.

The goods are entered at 160°–170° F. and worked for 10–15 minutes at this temperature; the dyestuff (2–7 per cent.), dissolved in water, is then added, the temperature raised to the boil, and a further 4–5 per cent. sulphuric acid added, after which the dyeing is continued at the boil for about 1½ hours. In some cases a more gradual addition of acid is advisable; on the contrary, pale shades may be dyed with the whole of the acid (4–6 per cent.) added at the outset. Wash well after dyeing and dry.

Dyeing of Direct Colours.—Direct colours may be dyed on wool in either neutral or faintly acid baths. In the latter respect the colours resemble Acid colours, but under acid conditions the wool fabric absorbs the dyestuff at a very rapid rate and great care must be exercised to avoid uneven dyeing, especially in the case of chlorinated material. Sulphuric acid must never be used, since it invariably yields uneven shades. As a rule the Direct colours are dyed with an addition of 2–5 per cent. acetic acid, or 5 per cent. ammonium acetate, which latter gradually dissociates with liberation of acetic acid, during the dyeing process. Very uneven dyeing colours may be dyed with Glauber's salt alone. Unlike cotton, wool has little or no affinity in the cold for Direct dyestuffs and, consequently, there is no point in starting the dyeing at a low temperature as for cotton. At the same time, regularity of shade is promoted by a gradual rise in the temperature of the bath from 150° F. to the boil, at which point the dyeing proceeds evenly until the bath is more or less exhausted of colour.

The usual procedure is to enter the goods into a bath (at 140°–150° F.) set with—

{ 1– 4 per cent. Direct dyestuff.
2– 5 ,, ,, acetic acid 12° Tw.
10–20 ,, ,, Glauber's salt.

The temperature is raised gradually during ¾ hour to the boil and dyeing continued at the boil for 1–1¼ hours. If the bath still contains dyestuff it may be exhausted by a further addition of 1–3 per cent. acetic acid, 12° Tw.,

added in small portions at a time according to requirements. The goods are then washed and dried.

DYEING OF METACHROME COLOURS, ETC.—Woollen goods intended for dyeing by the Metachrome process ought to be as neutral as possible; any mineral acid retained by the cloth from the chlorinating or bleaching processes must be removed before dyeing by a treatment with dilute ammonia ($1\frac{1}{2}$–2 per cent. ammonia, 25 per cent. on the weight of the cloth) at 75°–85° F., followed by a thorough wash. In the presence of free mineral acids the dyestuffs are absorbed at so rapid a rate that uneven dyeing results.

According to the depth of shade desired, the dye bath is set with—

$1\frac{1}{2}$– 5	per cent.	dyestuff.
10	,, ,,	Glauber's salt.
2 – 5	,, ,,	Metachrome mordant (previously dissolved at the boil).

The goods are entered at 95°–105° F. and run at this temperature for 10–15 minutes; the bath is then raised to the boil gradually during 1 hour, and dyeing continued at this temperature for a further 1–$1\frac{1}{2}$ hours. The goods are then washed thoroughly and dried.

Various other types of dyestuffs, *e.g.* Acid and Direct colours, in addition to Metachrome colours, are applicable by this process, which increases their fastness to washing (*vide* list, p. 893).

As a rule, discharge effects on wool come out best on chlorinated material, and for dark grounds chlorination is almost a necessity. Where the ground colour levels easily, it can be dyed on chlorinated material to considerable advantage—amounting in some cases to a saving of 25 per cent. of dyestuff. On the other hand, dyestuffs that tend to give uneven shades are better dyed on untreated wool, the material being treated in chlorine afterwards. Many of the Acid colours given in the first list on page 893 will withstand a run through the chlorinating baths and may, therefore, be used for the production of compound shades with colours that do not dye up well on chlorinated cloth (Anthracene acid browns, Lanacyl blue R., etc.). Though chlorination is not absolutely essential, it offers undoubted advantages in most instances.

DISCHARGING AGENTS.—White and coloured discharges are obtained on grounds dyed according to the preceding methods by means of reducing agents only—hydrosulphites of various brands, stannous salts, and mixtures of metallic zinc powder with bisulphites. Of these the most important are the hydrosulphites or sulphoxylate-formaldehyde compounds, which are applicable to a wider range of grounds and yield purer whites and better results generally than other discharging agents.

As a rule the tin (stannous) discharges do not give good whites owing to the difficulty of removing the products of the reduction process from the wool fibre without impairing the quality of the print; but for coloured effects they are still used to a considerable extent, and in some cases, too, they produce quite satisfactory white discharges, *e.g.* on grounds of Azo acid blues, Victoria violets, Flavazine, blue shades of Victoria scarlet and analogous dyestuffs. The best and most reliable whites, however, are given by hydrosulphites, with or without additions of zinc oxide or other plastic bodies.

The zinc-bisulphite discharge is no longer in current use except for a few special block-printed styles which can be produced as well by more convenient means. It was always a difficult process to work by machine by reason of the fact that the zinc powder was exceedingly apt to stick in the engraving of the printing rollers and thus give rise to imperfect discharges. It was really a sort of hydrosulphite discharge, and since the introduction of stable hydrosulphite compounds its use has become unnecessary.

(1) Hydrosulphite Discharges.

Sulphoxylate-formaldehyde compounds not only produce much purer whites on wool than tin salts, but they also discharge readily many colours which effectually resist the reducing action of tin. For coloured discharges they are equally suitable, and for this purpose may be associated with Eosines, Acid colours, Basic dyestuffs, and, occasionally, with Mordant colours of the Modern and Gallo series, Prune pure, etc.

White Discharges.—Although fairly good white discharges may be obtained from sulphoxylate alone, it is usual to improve their appearance by the addition of zinc oxide, blanc fixe, titanium oxide, or even China clay, which may be fixed or not, as desired, by means of egg albumen. These pigments, by forming a white covering on the surface of the discharged portions, effectually disguise the natural yellow tinge of the wool fibres. Intimate mixtures of sodium formaldehyde-sulphoxylates with zinc oxide, prepared specially for discharge printing on wool, are found on the market under the names of Formosul C.W., Rongalite C.W., Hydraldite C.W. extra, Hydrosulphite R.W.S. Ciba, etc., all of which are convenient in use rather than essential. The presence of zinc oxide (and other plastic bodies) in discharge pastes has the further effect of activating the reducing action of sulphoxylates during steaming and, simultaneously, prevents the colour from running into the unprinted parts of the ground.

In making up discharge pastes care should be taken to avoid using more than a slight excess of sulphoxylate over the quantity required to discharge the ground shade; under the influence of steam the wool fibre is sensitive to the action of sulphoxylate, and any considerable excess is liable to damage it. To some extent the fibre may be protected by additions of glycerine, acetine, or diethyl tartrate (Developer D.), which also prevent it from becoming brittle during steaming and preserve its softness and suppleness.

White Discharges.

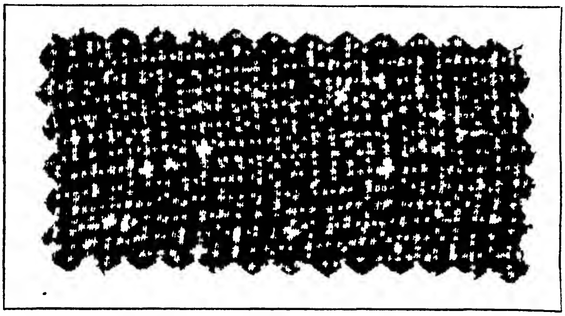
	A.	B.	C.	D.	E.
	grms.	grms.	grms.	grms.	grms.
Neutral British gum 1:1	500	..	380	..	500
„ starch-tragacanth paste	..	500	..	..	..
„ industrial gum 1:2	..	..	..	330	..
Zinc oxide	100	150	..	100	..
Titanium oxide, "Kronos"	..	..	100	..	..
Water	170	75	130	100	..
Acetine N.	..	..	..	50	..
Glycerine	..	..	80	50	100
Rongalite C.W. (Formosul C.W.)	..	..	..	250	..
Formosul	200	200	200	..	..
Hydrosulphite R.W.S. Ciba	..	..	..	..	300
Egg albumen 50 per cent. solution	..	75	60	60	100
Sodium bisulphite 72° Tw.	..	..	..	30	..
Turpentine	30	..	..	30	..
Aniline oil	..	..	50	..	..
	1000 grms. each.				

In these recipes, which are typical of the various compositions used in practice, the quantity of hydrosulphite must be increased or decreased accord-

ing to the discharging properties and depth of shade of the ground colour. As given they are suitable for most of the dark shades usually demanded. If a colour is very difficult to discharge and gives a poor white, it is unsuitable for the style and ought to be replaced by a more amenable dyestuff.

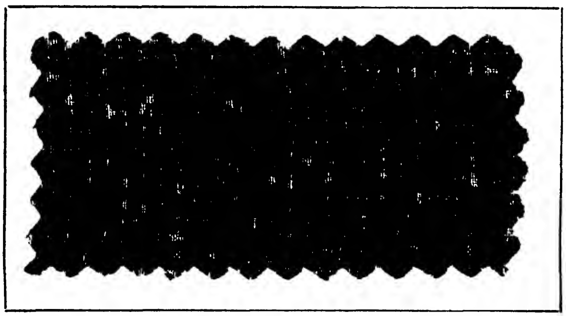
The following printed patterns are not intended to illustrate the brightest effects obtainable in wool discharge styles, but to serve as examples of the sounder work produced to-day with dyestuffs of recent introduction, of different groups, of different methods of application and of excellent all-round fastness.

The first five patterns are dyed with Neolan colours according to the methods already described.



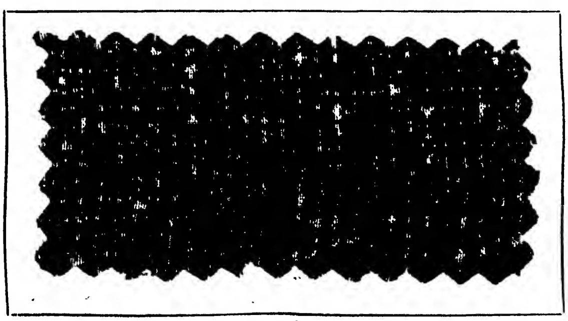
(S.C.I.B.)

2 per cent. Neolan Orange G.R.E. — discharged with 250 grms. Hydrosulphite R.W.S. Ciba per kilo. printing colour.



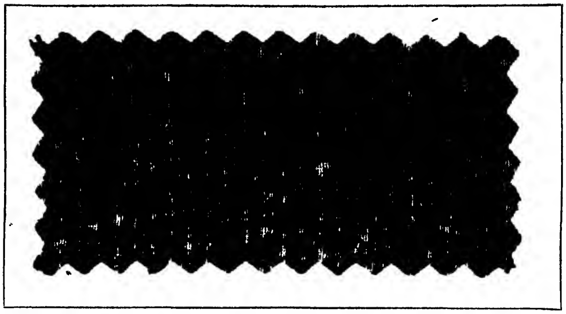
(S.C.I.B.)

1·5 per cent. Neolan Blue G.G.
1·5 „ „ Yellow G.
3·0 „ „ Red B.R.E.
} discharged as above.



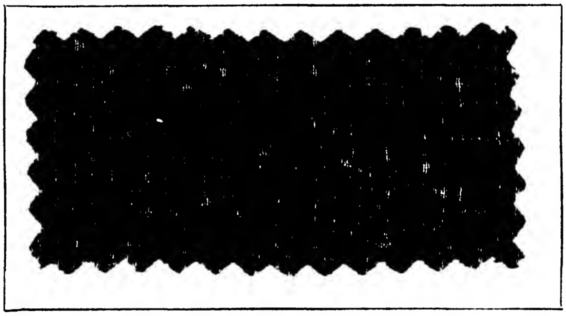
(S.C.I.B.)

4 per cent. Neolan Bordeaux R.: discharged as above.



(S.C.I.B.)

3 per cent. Neolan Green B.L. conc.: discharged as before.



(S.C.I.B.)

3 per cent. Neolan Navy Blue R.B.A.: discharged as before.

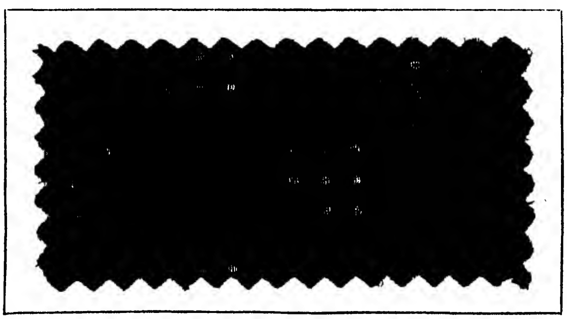
The discharge used for these patterns is as follows :—

250 grms. Hydrosulphite R.W.S. Ciba.
570 ,, starch-tragacanth paste.
80 ,, glycerine.
100 ,, egg albumen 50 per cent. solution.

1000

Print on the foregoing Neolan dyeings, steam for 5 minutes at 214° F. in the rapid ager, wash well and dry.

The ever-popular black and white article of excellent quality may be obtained by discharging dyeings of Neolan or Palatine Fast blacks. Thus :—



(I.G.)

Dye: 8 per cent. Palatine Fast Black R.R.N.
Discharge: 200 grms. Rongalite C. per Kilo. (Discharge I.G.).

The chlorinated cloth is dyed with—

$\begin{cases} 8 \text{ per cent. Palatine Fast black R.R.N.} \\ 10 \quad ,, \quad \text{sulphuric acid 168° Tw.} \end{cases}$

at the boil for 1½–2 hours, then washed thoroughly in hot and cold water to remove as much acid as possible, neutralised with weak ammonia, if necessary, washed, dried, and printed with—

Discharge I.G.

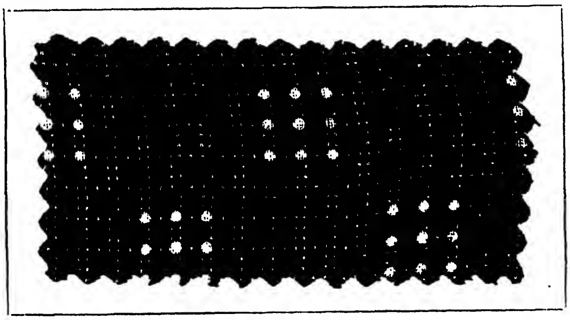
150–200	grms.	Rongalite C. or Formosul.
180–130	,,	water.
100	,,	titanium dioxide, "Kronos."
380	,,	British gum 1 : 1.
80	,,	glycerine.
50	,,	aniline oil.
60	,,	egg albumen 50 per cent. solution.
1000		

After printing dry carefully, steam for 5 minutes at 214° F. in the rapid ager, wash thoroughly, and dry.

For all discharge styles on wool the steam must be moist. The drying of the washed goods after steaming is preferably carried out on a stenter.

Other fast grounds are produced by dyeing certain Acid colours, Direct colours, and Acid Mordant colours by the Metachrome process as previously noted and described.

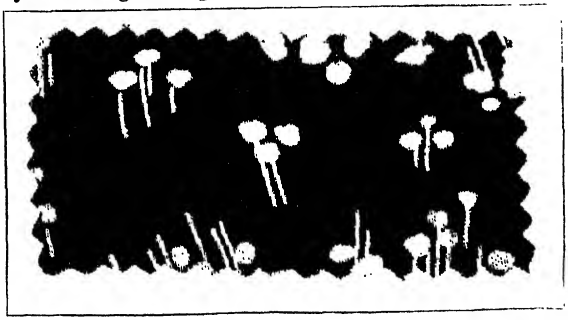
Diamine fast red F. is one of the best Direct colours for this mode of working.



(I.G.)

Dye $\begin{cases} 2 \text{ per cent. Diamine Fast Red F.} \\ 3 \quad ,, \quad \text{Metachrome mordant.} \end{cases}$ Discharged with Discharge I.G.

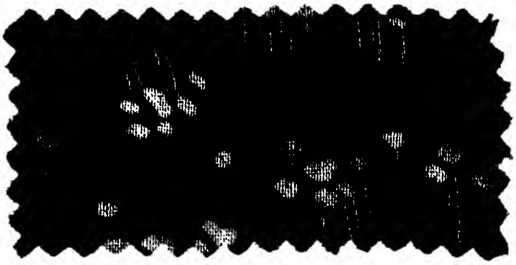
Amongst the Acid dyestuffs, Supranol red B.R. and Supranol orange G.S. both yield easily dischargeable grounds of superior fastness.



(I.G.)

Dye $\begin{cases} 1{\cdot}5 \text{ per cent. Supranol Orange G.S.} \\ 3 \quad ,, \quad \text{Metachrome mordant.} \end{cases}$ White: Discharge I G.

Various dark shades of brown, olive, and blue, and also blacks, of good general fastness to washing, light, and sea-water, etc., are obtained from Acid Mordant and Metachrome dyestuffs used either singly or in admixture. A navy blue of this type is illustrated below—



(I.G.)

Dye $\left\{\begin{array}{l}\text{2·5 per cent. Anthracene Chrome Blue R.W.N.}\\ \text{3 ,, Metachrome mordant.}\end{array}\right\}$ White: Discharge I.G.

After printing with the discharge, these Metachrome dyeings are steamed and washed as described for Neolan and Palatine Fast colour dyeings.

Much brighter grounds than those displayed in the preceding patterns are obtainable in immense variety from the ordinary Acid dyestuffs. Such grounds, however, are of inferior fastness, being suitable only for goods that are not required to withstand repeated washing, though generally good to light.

Coloured Discharges.—With very little modification most of the hydrosulphite discharges used for cotton, except those with Vat and Sulphur colours, are suitable for printing on wool. Many Acid colours, too, are resistant to the action of hydrosulphites and, where they can be used, they are to be preferred to Basic dyestuffs, which are not very fast to rubbing. The Basic dyestuffs are usually applied without tannin, but an addition of tannic acid improves their fastness to rubbing and washing, although it dulls the shades slightly. The Mordant colours are employed only for dark blues and greys in cases where good fastness to washing is required. Dyestuffs of the Eosine type, and Rhodamines, are largely used for pinks and reds, no other dyestuffs giving equally brilliant shades.

General Recipes for Coloured Discharges.

	I.	II.	III.	IV.
	grms.	grms.	grms.	grms.
Dyestuff	25	25–30	25–30	25
Glycerine	60	70	60	60
Water	100	150	110	100
Starch-tragacanth paste	450	500	400	215
China clay 1:1	..	..	100	..
Formosul or Rongalite C.	200	..	200	..
Hydrosulphite R.W.S. Ciba	..	250	..	..
Water	165	..	100	..
Tannic acid 50 per cent. solution	..	..	..	100
Discharge Paste W.A.	..	..	..	500
Make up to	1000 grms. each.			

DISCHARGE PASTE W.A.

25	grms.	starch.
85	,,	water.
400	,,	tragacanth mucilage 40 : 1000.
90	,,	aniline oil.

Boil, cool to 120° F., and add—

400 grms. Formosul or Rongalite C.

1000

Recipes I., II., and III. are suitable for all the colouring matters in the following list; recipe IV. is specially for Basic colour discharges of superior fastness. By omitting the tannic acid recipe IV. becomes an alternative to I., II., and III. for Acid and Basic colours.

The following are amongst the most important of the many dyestuffs available for the production of coloured discharge effects on woollen goods dyed with Acid, Direct, and Acid Mordant dyestuffs (see previous lists of dischargeable ground colours):—

ACID COLOURS.		BASIC COLOURS.	
Quinoline yellow A.S.	(I.C.I.)	Acronol yellow T.S.	(I.C.I.)
Eosine Y.S.	(,,)	Acridine orange R.S.	(,,)
Phloxine B.S.	(,,)	Rhodamines B., 6 G.D.N.S.	(,,)
Indulines A.S., 2 B.S., 5 B.S.	(,,)	Methylene blue N.S.	(,,)
Nigrosines G.S., R.S.	(,,)	Thioflavine T.	(I.G.)
Wool fast blues B.L., G.L.	(I.G.)	Flavophosphines, all brands	(,,)
,, ,, violet B.	(,,)	Rhoduline yellow 6 G.	(,,)
Formyl violet S. 4 B.	(,,)	Thionine blue G.O.	(,,)
Fast blues R., 3 R.	(,,)	Rhodamine 6 G.H. Extra	(,,)
Brilliant Kiton red B.	(S.C.I.B.)	Nile blue	(,,)
Erythrosine B. 818	(,,)	Discharge navy blue S. Extra	(,,)
		Acridine orange D.H.	(D. & H.)

Colours of less well-known names, by other makers, analogous to or identical with the foregoing, are also suitable for coloured discharges, but they are too numerous and not sufficiently interesting to mention individually; their employment is mainly dictated by price.

Greens and other compound shades are obtained from mixtures. It is advisable to confine mixtures to colours of one class; Acid and Basic dyestuffs mutually precipitate each other in many instances, and it is well to avoid such risks of loss.

The rarely used *Mordant Colours* are applied by methods similar to those employed for hydrosulphite discharges on cotton goods. They are useful colouring matters where fast dark blues or greys are required, but are otherwise unimportant. Amongst the most commonly used may be noted Modern blues and violets, Celestine blue B., Ultracyanine, Chrome violet blue, Chromoglaucine V.M., various members of the Gallo series, and even Persian berries. Example:—

NAVY BLUE V.M.

$$\left\{\begin{array}{rll} 50 & \text{grms.} & \text{Chromoglaucine V.M. paste.} \\ 50 & ,, & \text{glycerine.} \\ 150 & ,, & \text{water.} \\ 150 & ,, & \text{tragacanth mucilage 60 : 1000.} \end{array}\right.$$

Dissolve, cool, and add—

$$\begin{array}{rll} 100 & \text{grms.} & \text{chromium acetate } 32^\circ \text{ Tw. (neutral).} \\ \left\{250\right. & ,, & \text{Formosul C.W.} \\ \left.250\right. & ,, & \text{starch-tragacanth paste.} \\ \hline 1000 & & \end{array}$$

Rongalite C. or Formosul C. may replace Formosul C.W. in this recipe if desired, and Developer D. (diethyl tartrate) or Acetine N. may also be used in place of glycerine or a portion of the water.

Steaming of Coloured Discharges.—The goods, after printing, are gently dried, allowed to lie an hour or two to cool and condition, and then steamed for 5–6 minutes in the rapid ager with damp steam at 212°–214° F. This steaming effects the discharge proper, but in order to fix the colours satisfactorily, the goods are steamed for a further 30 minutes between damp greys and without pressure in a cottage steamer or in the Mather and Platt continuous automatic steaming and ageing machine. The goods are then thoroughly washed in the open width, squeezed and dried (preferably) on a stentering machine.

(2) TIN DISCHARGES ON WOOLLEN FABRICS.

The relative merits of tin and hydrosulphite discharges in general have been discussed already under the heading "Discharging of Direct Cotton Colours." It may be repeated here, however, that tin discharges, though much less used than formerly, are still of importance in cases where an air-free hydrosulphite steam ager is not available. Moreover, tin discharges possess the advantage of being comparatively stable after printing—a property of considerable value to hand-block printers in that it permits of the printed goods being allowed to lie for several days, without detriment, before steaming.

The wool fibre resists the destructive action of acid stannous salts much better than the cotton fibre, and consequently it is possible to use more concentrated discharge pastes, with a corresponding gain in the quality of the discharge effects generally.

In addition to stannous chloride ("tin crystals"), which forms the basis of most tin discharges, the following ingredients are used in the printing pastes: tartaric, citric, oxalic, or glycollic acid, glycerine, acetine, ammonium sulphocyanide, and sodium acetate. Excess of sodium acetate must be avoided; the wool fibre is affected less in steaming by free organic acids than by the alkali set free from a large amount of sodium acetate.

Whilst coloured discharges are readily obtainable, it is always difficult to obtain pure whites with tin discharges, owing to the formation of coloured reduction products which resist all efforts at removal. For this reason white

discharges are rarely attempted, except on light grounds of Acid dyestuffs and medium grounds of Direct dyeing colours. When combinations of white and colours are required, the white is preferably obtained, if possible, by printing hydrosulphites, although, if the object be small, stannous chloride may be employed, as in such a case the white stands out sufficiently well by contrast with the ground and neighbouring discharge colours.

WHITE DISCHARGES of different concentrations are employed according to the depth and properties of the ground colour, the strength of the engraving, and the duration of the steaming process. These factors vary considerably, and it is possible to give examples of only a few practical recipes, which may of course be modified as required.

WHITE DISCHARGES (STANNOUS CHLORIDE).

	A.	B.	C.	D.	E.	F.
	grms.	grms.	grms.	grms.	grms.	grms.
Acid starch paste 12½ per cent.	500	500	500	..	..	..
,, ,, ,, 20 ,, ,,	..	..	..	525	..	..
British gum solution 1:2	120	75	50	..	..	..
Senegal ,, ,, 1:1	..	..	..	..	550	600
Stannous chloride	250	250	250	350	200	240
Water	100	50	65	..	100	75
Glycerine	..	..	..	..	50	..
Sodium acetate	30	125	..	90	60	60
Ammonium sulphocyanide	..	..	85	..	..	..
Citric acid	..	..	50	35	..	..
Tartaric acid	..	..	..	..	40	25
	1000 grms. each.					

These discharges are suitable for full shades of any dyestuffs which are dischargeable with tin salts. (A), (B), (C), and (F), after printing, are steamed for 10 minutes without pressure, or twice, for 5 minutes each time, through an Aniline black rapid ager; (D) is used only for very finely engraved lines or spots, etc., and is also steamed for about 10 minutes; (E) is well adapted for a longer steaming of ½–1 hour, and is the type of white discharge used in multicolour discharge styles. All may be used for light grounds, or long steaming, if reduced in strength by an addition of acid thickening.

Another recipe suitable for prolonged steaming is made up as follows:—

DISCHARGE WHITE S.A.

750 grms. stannous acetate 28° Tw.
50 ,, tartaric acid.
150 ,, wheat starch.
50 ,, British gum powder.

1000

Boil and cool.

Print, steam for 1 hour without pressure, wash, and dry.

COLOURED DISCHARGES are most conveniently prepared by adding solutions of Acid or Basic dyestuffs to a standard discharge paste containing the necessary stannous chloride, sodium acetate, and citric acid, the last being better for general purpose coloured discharges than other organic acids. The thickenings employed may be either starch and British gum mixtures or British gum alone, or natural gums—Senegal, Kordofan, Ghatti, etc.—alone. The natural gums are most suitable for large objects, as they wash out easily. Starch thickenings are useful for small objects and, where possible, are to be preferred for Basic colour discharges, because they hold the colour better than gums.

STANDARD PASTES FOR COLOURED TIN DISCHARGES.

	D 1.	D 2.	D 3.	D 4.	D 5.
Water	..	2460	..	390	..
Gum Senegal 1:1	3720	..	..	..	..
Stannous acetate 30° Tw.	..	..	2880	3000	4650
Wheat starch	..	900	900	900	900
Light British gum	..	450	300	..	300
Acetic acid 12° Tw. (50 per cent.)	..	..	..	600	..
{ Citric acid (powdered)	180	180	180	..	150
{ Water	240	210	240	..	..
Boil, cool a little, and add—					
Stannous chloride	1500	1440	1200	900	..
Sodium acetate	360	360	300	210	..
	6 kilos. each.				

COLOURED DISCHARGES (WITH PRECEDING STANDARD PASTES).

	A.	B.
{ Acid or Basic dyestuff	20–30 grms.	20–30 grms.
{ Acetine, Fibrit D. or Glycine A.	50 „	..
{ Water	150 „	150 „
Dissolve by heat and add—		
Gum Senegal 1:1	170 „	..
Acid starch paste	..	220 „
Warm together, cool to 80°–90° F. and add—		
Standard Discharge Paste D 1	600 „	..
„ „ „ D 2, 3, 4 or 5	..	600 „
Make up to	1000 grms.	1000 grms.

(A) is suitable for nearly all Acid and Basic dyestuffs used in coloured tin discharges; (B) serves only for easily soluble dyestuffs, but in cases where starch thickenings are preferred for the work in hand, it may be made up on the lines of (A) by simply adding Acetine, etc., and reducing the starch thickening *pro rata*.

If desired, discharge colours may be made up directly, as indicated in the following table:—

Coloured Discharges (Stannous Chloride).

	Red.	Yellow.	Blue.	Green.	Violet.	Pink.
	grms.	grms.	grms.	grms.	grms.	grms.
Eosine G.G.F.	75	..	..	..	..	..
Quinoline yellow O.	..	50	..	..	..	..
Phloxine S.	25	..	..	..	..	30
Victoria blue B.	..	..	20	..	..	..
Brilliant green	..	..	..	7½	..	..
Thioflavine T.	..	..	..	22½	..	..
Methyl violet	..	..	..	..	10	..
Boiling water	175	150	180	170	190	170
Acid starch paste	..	525	525	525	525	..
Citric acid	25	25	25	25	25	25
Gum Senegal 50 per cent.	275	..	..	..	..	325
British gum	100	..	..	..	..	100
Sodium acetate	50	50	50	50	50	50
Stannous chloride	150	150	150	150	150	150
Water	125	50	50	50	50	150
	1000 grms. each.					

These recipes represent the general methods of applying Acid and Basic dyestuffs to the production of tin salt discharge effects on dyed woollen fabrics. Other selected members of the same two groups are also applicable by similar means. Of these a few are listed below.

Dyestuffs Suitable for Tin Salt Discharges.

Acid Dyestuffs.

Quinoline yellows, all brands.
Formyl blue B.
Alkali blues, various brands.
Cyanol F.F.
Patent blues, all brands.
Brilliant milling blue B.
Eosines, all brands.
Phloxines, ,,
Erythrosine.
Rose bengale.
Sulphorhodamines B., G.
Acid violets, various brands.
Formyl violet S. 4 B.
Brilliant milling green B.
Brilliant acid green 6 B.
Cyanol greens B., 6 B.
Nigrosines (water-soluble).
etc.

Basic Dyestuffs.

Thioflavines T., T.C.N.
Rhoduline yellow 6 G.
Flavophosphines.
Acridine orange D.H.
Victoria blues.
Acetine blues.
Setocyanine.
Setoglaucine.
New methylene blues.
Rhodamines B., 6 G.H. Extra.
Astraphloxine F.F. Extra.
Safranines.
Astra violet F.F.D. Extra.
Methyl violets.
Malachite green.
Brilliant green.
etc.

Process.—Discharge printing colours, made up with the above dyestuffs according to the foregoing recipes, are printed on chlorinated woollen delaines, etc., dyed with suitable dischargeable ground shades (see list hereafter). After printing, the goods are gently dried, allowed to lie until they have regained their natural moisture, and then steamed for ½–¾ hour *without* pressure; a

steaming of 10 minutes or less is often sufficient to effect the actual discharging of the dyed ground, but the longer treatment effects a better fixation of the printed discharge colours. After steaming, the goods are thoroughly washed in water, soured and washed again, if necessary, and dried.

Very fine red and blue styles are produced by first dyeing the wool in a dischargeable Acid red and then printing over it a blotch pattern in a discharge navy blue; red and dark green may be obtained by the same method. The following are examples of this style.

Ground Shade.—Dye chlorinated wool (delaine) $2\frac{1}{2}$ per cent. Brilliant cochineal 2 R., with addition of acetic acid and Glauber's salt. Wash, dry, and print Discharge blue or green below.

Discharge Blues and Green.

	Blue R.	Blue G.	Green.
	grms.	grms.	grms.
Formyl Violet S. 4 B.	25	25	..
Acid Green extra conc.	25	35	..
Naphthalene Green V.	..	..	50
Water	250	240	75
Acetic acid 9° Tw.	..	..	175
Stannous acetate 28° Tw.	500	500	500
British gum	100	100	100
Starch	75	75	75
Citric acid	25	25	25
	1000 grms. each.		

After printing, steam for $\frac{3}{4}$-1 hour without pressure, wash well, and dry.

As in the case of hydrosulphite discharges, it is advisable to use Acid dyestuffs wherever possible for coloured tin salt discharges. When Basic dyestuffs are employed, the goods require very careful washing in order to prevent the printed discharges from marking-off and thus soiling the ground shade.

Dischargeable Grounds.—Grounds dyed on wool with the following dyestuffs are all readily discharged with stannous salts—

Acid Dyestuffs.

Tartrazine.
Flavazines, all brands.
Palatine light yellow R.
Fast acid yellow T.L.
Milling yellow O.
Oranges II., G.
Sulphon orange 5 G.
Tropæolines O., O.O., G.
Crocein scarlet 7 B.
Amidonaphthol reds.
Ponceaux 2 R.L., F.R., F.F.R.
Brilliant lanafuchsine S.L.
Azo acid violet A.L.

Direct Dyestuffs.

Cotton yellow G.I.
Chrysophenine G.
Benzo fast yellow 5 G.L.
Benzo light orange 2 R.L.
Geranine B.B.
Oxamine red 3 B.
" fast pink B.
Chlorazol fast red K.S.
" pink B.K.S.
" bordeaux 6 B.S.
" fast helios, K.S., 2 R.K.S.
" fast blue F.F.S.
Brilliant fast blue B.

Acid Dyestuffs—*continued.*	Direct Dyestuffs—*continued.*
Azo wool violet 7 R.	Chlorazol fast black B.S.
Victoria violets 4 B.S., R.L.	Benzo dark greens B., G.S.
Brilliant sulphonazurine R.	Diamine green G.
Azo acid blue B.	Direct deep black E.W. Extra.
Sulphon acid greens B., 2 B.L.	
Naphthylamine black 4 B.	
,, ,, E.F.F.	

and many others, of similar constitution, too numerous to mention.

(3) Sulphite Discharges.

Heilmann and Battegay (*Journ. Soc. Dyers and Colourists*, 1906, p. 234) have pointed out the suitability of sulphite of potash for the production of discharges on woollen goods, and their experiments proved that certain Acid colours are extremely sensitive to the action of this reagent.

They found that sulphite of potash discharges, amongst others, the following colours: Azo acid red, Domingo blue, Scarlet 5 R., Tartrazine, Half-wool scarlet 4 B., etc.

By a short run through the rapid ager, Domingo blue yields half-discharge effects, but perfect whites are obtained by prolonging the steaming for 30 to 35 minutes without pressure.

Various effects are obtained by dyeing the wool with mixtures of dischargeable and non-dischargeable colours, and also by the direct printing of coloured sulphite of potash pastes.

The following examples are typical of these Sulphite Discharges:—

White:—700 grms. sulphite of potash 90° Tw.
200 ,, British gum paste.

Heat, cool, and add—

50 grms. acetate of soda.
50 ,, water.

1000

Coloured Discharges.

	Yellow.	Red.	Blue.	Green	Violet.
Milling yellow O.	50	..	..	30	..
Rhodamine 4 G.	..	35	..	..	..
Safranine O.	..	15	..	..	..
Cyanol extra	..	..	12	10	..
Formyl violet S. 4 B.	..	..	..	..	10
Water.	250	250	288	260	290
British gum.	200	200	200	200	200
Sulphite of potash 90° Tw.	500	500	500	500	500
	1000	1000	1000	1000	1000

On an experimental scale the above colours have given satisfactory results on grounds dyed with the Acid colours mentioned above. Great care, however, is needed in steaming, since, if the printed sides of the cloth happen by any means to come in contact with each other, the sulphite of potash marks off and partly discharges the colour of those parts of the cloth which ought to remain untouched.

Printing of Half-Wool or Union Goods.

Goods consisting partly of wool and partly of cotton are bleached and chlorinated in much the same way as all-wool goods. They are first well scoured at 40°–45° C. in a bath containing 3 grms. of soap and 5 grms. of ammonia soda per litre; then thoroughly washed until every trace of soap is removed, and finally bleached either by the peroxide of hydrogen process or by being stoved with sulphurous acid gas. The combined Peroxide and Bisulphite process, as described for pure wool, may also be employed with advantage. The chlorination and the preparation with tin salts are carried out in the usual manner. Sometimes half-wool goods are prepared with phosphate of tin. For this purpose they are padded in a cold solution of stannic chloride 4° Tw. (or oxymuriate of tin), allowed to lie rolled up for two or three hours, and then passed, without washing, into a cold or tepid 5 per cent. solution of sodium phosphate; finally, they are well washed and dried.

For the most part only the Acid, Basic, and Direct colours are used in half-wool printing; the Mordant colours find only a limited application, and then chiefly in combination with Basic dyestuffs, for the double purpose of increasing their brightness and their covering quality. The Direct colours are useful for direct printing, and also for the dyeing of ground shades intended for subsequent discharging.

After printing, the treatment of the goods is in most respects identical with that of all-wool fabrics. If, however, they contain a large amount of cotton they are damped, and then steamed in *dry* steam without pressure for ¾ to 1 hour; then washed and dried. Basic colours printed with tannin have to be run through tartar emetic (1 per cent. solution) to fix the colour on the cotton fibre.

PRINTING.—The cloth prepared as above is printed with colours prepared according to the following directions: the recipes are typical of those suitable for the different groups of dyestuffs usually employed:—

BASIC COLOURS.

20	grms.	Basic colour.
75	,,	acetic acid 9° Tw.
125	,,	water.
20	,,	tartaric acid.

Dissolve, and add to—

710	grms.	starch-tragacanth or gum Senegal thickening.
50	,,	50 per cent. solution of tannic acid in acetic acid.
1000		

Suitable for all Basic dyestuffs. Methylated spirits may replace wholly or in part the acetic acid if the colours are at all difficult to dissolve.

DIRECT COLOURS.

$\left\{\begin{array}{r}25\\350\\100\end{array}\right.$	grms. ,, ,,	Direct dyestuff. water. British gum.
350	,,	6 per cent. tragacanth thickening.
$\left\{\begin{array}{r}40\\135\end{array}\right.$	,, ,,	phosphate of soda. water.
1000		

For all Diamine, Titan, Mikado, Dianil, and Chlorazol colours, and for Erika, Chicago blue, Geranine, and other direct dyestuffs.

ACID COLOURS.—The Acid colours used for half-wool are identical with those employed for pure wool. Having no affinity for the cotton fibre, their fastness on half-wool depends upon the amount of pure wool present in this mixed fabric.

BLACKS AND DARK OUTLINES ON HALF-WOOL.

Blacks and dark colours generally are obtained with Logwood, and Mordant colours toned with Basic colours containing tannin.

BLACK.—Logwood with iron and chromium mordants.

CHOCOLATE.—Persian berries, Magenta, and Methyl violet or Brilliant green, with tannin and chrome mordant.

DARK NAVY.—Logwood (a little), Methyl violet, and Brilliant green, with chromium acetate and tannin.

BRIGHT NAVY.—Marine blue with a very little Brilliant green.

The Direct colours are also used at times for other dark shades, but usually they are reserved for medium and light colours.

Discharging on Half-Wool.—Discharge effects on half-wool materials are obtained by printing tin or hydrosulphite discharges on colours dyed with Direct dyestuffs.

The best and surest method of securing level ground shades is that of padding the goods through a padding machine containing dye liquors prepared on the following types:—

PADDING LIQUORS FOR DIRECT COLOUR DYEING.

	LIGHT BLUE.	DARK BLUE.	NAVY.	PINK.	YELLOW.	BROWN.
Diamine sky blue F.F.	10	..	..	..	..	..
Dianil blue R. . .	..	..	50	..	..	..
Titan pink or Erika .	..	..	..	25	..	..
Dianil yellow R. .	..	..	..	..	10	..
Chicago blue . .	..	25	..	..	..	..
Dianil brown 2 G. .	..	..	..	..	..	15
Water	920	885	860	885	920	915
Phosphate of soda .	20	40	40	40	20	20
6 per cent. tragacanth	50	50	50	50	50	50
	1000	1000	1000	1000	1000	1000

HELIOTROPE = Mixtures of Pink and Blue.
GREEN = ,, ,, Yellow and Blue.

Pad, dry, and print with discharge colours as under:—

DISCHARGE WHITE.

600 grms. acid starch-tragacanth paste.
200 ,, stannous chloride.
20 ,, citric acid.
180 ,, ammonium sulphocyanide.

1000

DISCHARGE RED.

25	grms.	Rhodamine 6 G. extra.
10	,,	Safranine A.N. extra.
150	,,	acetic acid.
200	,,	water.
150	,,	light British gum.

Boil, cool, and add—

80	grms.	Persian berries extract 50° Tw.
50	,,	sulphocyanide of ammonia.
200	,,	tin crystals ($SnCl_2$).
75	,,	acetic acid tannin solution 50 per cent.
60	,,	glycerine and water 1:1.
1000		

BRIGHT BLUE.

20	grms.	Thionine blue G.O.
150	,,	acetic acid.
15	,,	citric acid.
100	,,	water.

Dissolve, and add—

190	grms.	water.
120	,,	wheat starch.
25	,,	glycerine.

Boil, cool, and add—

80	grms.	ammonium sulphocyanide.
200	,,	stannous chloride.
100	,,	acetic acid tannin solution 50 per cent.
1000		

This last recipe serves for Rhodamine, Auramine, Thioflavine T., Brilliant green, Malachite green, Methyl violet, Methylene blue, and mixtures of these and of all other Basic dyestuffs, so that all varieties of compound shades are easily obtainable.

For dark blue blotches on red grounds the cloth is dyed and printed as under:—

(1) Dye the goods with 2 per cent. Diamine scarlet B. with an addition of phosphate of soda and Glauber's salt; wash well, dry, and—

(2) Print with the following blue:—

DARK BLUE S.D.

30	grms.	Methyl violet B.
25	,,	Victoria blue B.
10	,,	Brilliant green.
175	,,	acetic acid 9° Tw.

Dissolve, and add—

400	grms.	gum Senegal solution 50 per cent.
50	,,	British gum.

Boil, cool, and add—

30	grms.	Persian berries extract 50° Tw.
60	,,	ammonium sulphocyanide.
150	,,	stannous chloride.
30	,,	tannic acid.
30	,,	acetic acid 9° Tw.
10	,,	glycerine.
1000		

After printing on half-wool cloth dyed with Direct colours, all the foregoing discharges are steamed for 3–4 minutes in the rapid ager. The goods are then passed in the open width through a 1 per cent. solution of tartar emetic, well washed and dried. If the discharge is imperfect, a second run through the ager is usually sufficient to rectify it.

The same *hydrosulphite discharge process* that is employed for all-wool fabrics is equally suitable for half-wool materials, with the subsequent employment of the tartar emetic bath.

Of the many Direct colours available, those of the Chlorazol Fast series are particularly adapted for the dyeing of dischargeable ground shades on woollen fabrics. They are of excellent fastness to light, and, with a few exceptions, they yield good whites with hydrosulphites.

PART X.

SILK AND HALF-SILK PRINTING.

SILK AND HALF-SILK PRINTING.

In so far as its behaviour towards colouring matters is concerned, the silk fibre so closely resembles the wool fibre that the printing of silk fabrics presents but little variation from the printing of woollen fabrics. The main difference between the two processes lies in the preparation of the cloth, which, in the case of silk, consists only of mordanting the goods in stannic chloride or phosphate. The chlorination of silk does not increase the affinity of the fibre for colouring matters as it does in the case of wool.

The printing of silk, like that of wool, is restricted to the production of direct-printed and discharge and resist styles. The application of thickened mordants, followed by ageing, dunging, and dyeing, is inadmissible, on account of the staining of the silk fibres in the dye bath.

In addition to the Basic, Acid, Phthalein, Direct, and Mordant colours, all of which are suitable for silk printing, certain others, such as Aniline black, Nitroso blue, and Dinitroso-resorcin brown are also applicable, both for direct, discharge, and resist prints. The insoluble Azoic colours produced on the fibre are never employed, since they cannot be obtained sufficiently fast to rubbing.

Multicolour patterns, especially if they be heavy, are usually printed by block. Machine printing on silk is chiefly confined to single-colour patterns; for although silk has a greater affinity for most colouring matters than wool, it does not absorb thickenings so easily, and, consequently, these latter remain more or less on the surface of the cloth, and are extremely liable to smear during their passage under several rollers in quick succession. For this reason block printing is preferable to roller printing for patterns of two or more colours. Colours printed by block remain untouched by the application of subsequent colours, and therefore they are free from the tendency to smear and streak that is so much more troublesome in the printing of silk by machine than in that of other textile fabrics.

Nevertheless, many multicolour patterns on silk are printed by machine, and, with care, good results are obtained.

Whatever method of printing be adopted, the production of bright level colours depends upon the proper cleansing of the fibre. In order to ensure this, it is always advisable to scour the pieces before printing, however clean they may appear to the eye.

For this purpose they are soaped for 1–1½ hours at 35°–40° C. with 10 per cent. of their weight of neutral olive oil soap; then thoroughly washed and mordanted with tin. In the soaping, care must be taken to avoid the presence of free alkali, which would tend to injure the fibre.

Preparation in Tin.—Pad the goods, in a beck holding 1000 litres, with the following:—

$$\begin{cases} 50 \text{ litres stannic chloride } 140^\circ \text{ Tw.} \\ 950 \quad ,, \quad \text{water.} \end{cases}$$

After padding, wind the cloth on a wooden centre in the wet state, and

allow to lie thus for 4 hours ; then wash well, and dry on a stentering machine. Sometimes the tin is precipitated as phosphate before washing, in which case the padded goods are passed through a 5 per cent. solution of sodium phosphate and allowed to lie again for 2 hours, and finally thoroughly washed and dried.

When the silk is of a yellow tinge, it must be bleached before preparing with stannic chloride or any other tin salt. A good bleach is the following :—

After scouring in soap as above, work the pieces, in a stone pit, until saturated, in hydrogen peroxide liquor, and then allow to lie in the liquor until sufficiently white.

HYDROGEN PEROXIDE LIQUOR.

$\begin{cases} 50 \text{ litres hydrogen peroxide 10 vols.} \\ 200 \quad ,, \quad \text{water containing a little ammonia.} \end{cases}$

The bleaching will be effected in about 5 hours, after the lapse of which time the goods may be washed and treated in stannic chloride.

Printing.—In view of the fact that silk is printed by methods and with materials which are practically identical with those employed for the printing of wool, it is unnecessary to give more than a brief description of the application of the several types of dyestuffs and thickenings that come into consideration for silk and half-silk printing.

Of the colouring matters, the most widely employed are Acid dyestuffs of all descriptions, Basic dyestuffs (with or without tannin), and Direct dyestuffs of all the well-known groups. For the faster styles, the Mordant, Vat, and Indigosol colours are available and, for special work and Resist styles, Aniline and Diphenyl blacks are also of importance.

The best thickening agents to use for silk printing colours are those which wash out easily and completely, namely, gum Senegal, gum Arabic, gum tragacanth, and well calcined British gum. All these yield smooth, level shades. Gum tragacanth is especially appropriate for printing dark blotches, as it gives colours faster to washing than those thickened with other gums and, at the same time, leaves the material soft and elastic. For pale and medium blotches, gum Senegal and gum Kordofan stand alone and, although expensive, they give shades which are unsurpassed for purity, transparency, and uniformity. Starch and flour are useless in silk printing except for fine stipple work and small objects such as spots or delicate trails and outlines. Starch-tragacanth thickening is, however, frequently employed in the printing of Aniline and Diphenyl blacks. Very thin silk fabrics are best printed with British gum ; otherwise, after drying, they remain stiff and papery and are exceedingly liable to crack or tear during subsequent processes. British gum, being hygroscopic, absorbs a certain amount of moisture from the air and, consequently, if the printed and dried goods are allowed to lie for an hour or two, in a cool place, before undergoing further treatment, they lose their brittleness and become sufficiently supple to handle with safety.

[illegible]

The Acid dye[illegible] printing than any other class of co[illegible]s of good fastness to rubbing and o[illegible] but in most cases they cannot be re[illegible] although many of them are quite s[illegible]owever, possess an advantage over [illegible]ss into the white ground when washed in water. The Neolan and Palatine Fast dyestuffs come into a different category : they are unusually fast colours and may be ranked with the best Mordant dyestuffs, whether printed or dyed and discharged.

All Acid dyestuffs suitable for wool are equally applicable to silk printing and the list already given in the section on Wool Printing contains a small selection of appropriate colours. A further selection of printing colours of good fastness to light and water may be made from the Erio Fast colours (Geigy), the Xylene and Fast Sulphon colours (Sandoz), various soluble Nigrosines, and from many others which may be found by reference to the *Colour Index* of the Society of Dyers and Colourists and to the published lists of various manufacturers.

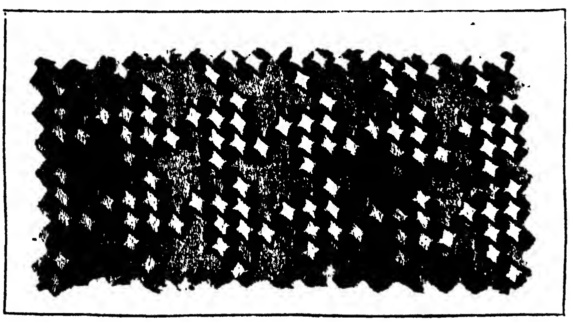
The formulæ tabulated below will be found to cover the application of all types of Acid dyestuffs :—

General Recipes for Acid Dyestuffs.

	I.	II.	III.	IV.	V.
	grms.	grms.	grms.	grms.	grms.
Acid dyestuff	40	40	40	80	60
Resorcin or glycerine	..	..	..	..	30
Water (boiling)	335	310	310	285	190
Glycerine	25	..	..	40	..
Ammonia 20 per cent.	..	..	..	25	..
Acetic acid 9° Tw.	..	50	50	..	..
Tragacanth mucilage 6 per cent.	550	..	..	..	..
Gum Senegal 1 : 1	..	275	275	500	650
British gum 1 : 1	..	275	275	..	..
Dissolve with heat, cool, and add—					
Tartaric acid 1 : 1	50	50	..	50	..
Ammonium oxalate (powdered)	..	..	..	..	20
Aluminium sulphate (powdered)	..	..	..	20	..
,, acetate 16° Tw.	..	..	50	..	..
Acetic acid 9° Tw.	..	..	..	..	50
	1000 grms. each.				

(I.) and (II.) are suitable for all ordinary Acid colours ; (III.) is recommended for various scarlets of the Ponceau, Crocein, and Brilliant crocein types ; (IV.) is a general recipe for Acid blacks, and (V.) is also for Acid blacks and, with less colouring matter (say 20–30 grms.), for most other Acid colours as an alternative to (I.) and (II.) (see p. 874).

Other recipes are given in conjunction with the following printed patterns.



(I.G.)

Yellow: Azoflavine 3 G. Extra Special 3 per cent.
Brown: Supramine Brown R. 3 per cent.

YELLOW.

30	grms.	Azoflavine 3 G. extra spec.
30	,,	Glyecine A.
220	,,	water.

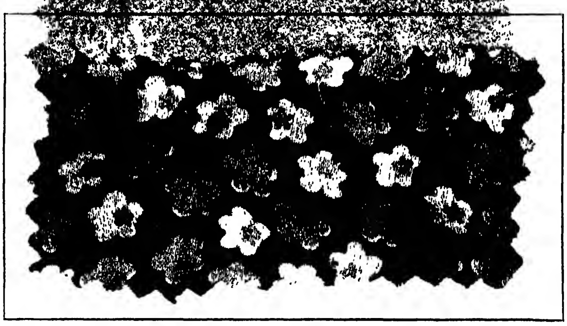
Dissolve and add—

650	,,	Senegal thickening 1 : 1.
20	,,	ammonium oxalate.
50	,,	acetic acid 9° Tw.
1000		

BROWN.

As yellow, but with Supramine brown B.

The same recipe has been used in producing the next two patterns, of which the light shades are obtained by an addition of reducing thickening.



(I.G.)

Red: Milling Red R. 3 per cent.
Pink: Milling Red R. 3 per cent., 1 : 3 (or 0·75 per cent.).

PINK.

{1 part Milling red R. 3 per cent. printing colour.
{3 parts reducing thickening (below).

REDUCING THICKENING.

700	grms.	Senegal thickening 1 : 1.
20	,,	acetic acid 9° Tw.
10	,,	ammonium oxalate.
10	,,	Glyecine A.
260	,,	water.
1000		

(I.G.)

Brilliant Indocyanine 6 B. 3 per cent. and 0·75 per cent.

In these recipes the oxalate of ammonia may be replaced by citric, tartaric, or acetic acid.

After printing on weighted or unweighted silk, the goods are steamed for 1 hour without pressure in a cottage steamer, and then thoroughly well washed in cold water and dried.

Much faster though somewhat less bright colours are obtained from the *Palatine Fast* and *Neolan dyestuffs*, especially when printed with a small proportion of chromium acetate. Thus—

(I.G.)

Palatine Fast Orange G.R.N. 5 per cent.

Palatine Fast Orange.

50	grms.	Palatine Fast orange G.R.N.
30	,,	Glyecine A.
30	,,	glycerine.
440	,,	water.
300	,,	British gum powder.

Heat together and add—

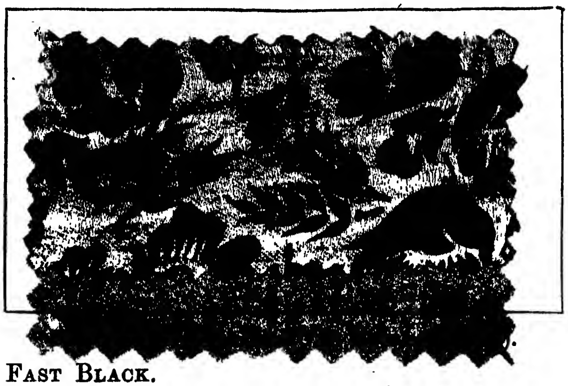
100 grms. acetic acid 9° Tw.

Cool and add—

50 grms. chromium acetate 32° Tw. (violet).

1000

The above re[illegible]ept blacks, which are printed at a higher concentration and may be reduced as required for grey shades (see following).



Palatine Fast Black.

60 grms. Palatine Fast black W.A.G.N.
30 ,, Glyecine A.
30 ,, glycerine.
400 ,, water.
300 ,, British gum powder.
100 ,, acetic acid 9° Tw.
80 ,, chromium acetate 32° Tw. (violet).

1000

After printing, steam for 1 hour without pressure, wash well in cold water and dry.

The *Neolan* dyestuffs, which are in reality the prototypes of the Palatine Fast group, produce results which are in every way equal to those obtained from the latter, and if desired may be printed in exactly the same manner. The patterns shown below have, however, been produced by a different recipe recommended by the makers.

Neolan Red G.R.E. 30 grms. per litre of printing colour (S.C.I.B.).

Neolan Red.

30 grms. Neolan red G.R.E.
370 c.c. boiling water.

Dissolve and stir into—

550 grms. British gum 1 : 1.

Cool and add—

40 c.c. chromium acetate 32° Tw.
10 ,, ammonium tartrate 32° Tw.

Bulk to 1000 c.c.

Other Neolan colours, up to 30 grms. per litre, as for example Neolan violet 5 R. illustrated h[illegible]re [illegible] the same way.

Neolan Violet 5 R. 30 grms. per litre (S.C.I.B.).

For dark shades, blacks, and less soluble members of the group, a slightly different procedure is adopted. The dyestuff is pasted up with water, mixed with dry British gum, and the whole boiled together until solution of the dyestuff is complete; the mixture is then cooled and the fixing agents added as per example below.

N[illegible]).

NEOLAN BLA[illegible]

50– 80 grms. Neolan dyestuff.
575–500 c.c. water (hot).
Mix, and add—
300–300 grms. British gum powder.
Boil, cool, and add—
60–100 c.c. chromium acetate 32° Tw.
15– 20 ,, ammonium tartrate 32° Tw.

Bulk to 1000 c.c.

After printing, steam for 1 hour without pressure, wash well in cold water, and dry.

The excellent fastness to light, washing, perspiration, sea-water, etc., of the Palatine Fast and Neolan colours makes them of particular interest for

the printing of silk dress goods, scarves, and other articles that are subjected to more than occasional wear and are required to undergo repeated washing.

(b) Basic Dyestuffs in Silk Printing.

The Basic dyestuffs are used principally in silk printing for styles in which extreme brilliancy is of first importance. They are inferior to the acid dyestuffs in fastness to light, but superior in fastness to water and washing, particularly so when printed with tannic acid. The addition of tannic acid, however, dulls the shades somewhat and it is usual to dispense with it.

Basic Dyestuff Printing Colours.

	I.	II.	III.	IV.
	grms.	grms.	grms.	grms.
Basic dyestuff	25	25	25	25
Water	275	200	200	225
Acetine	..	40	40	..
Acetic acid 9° Tw.	100	100	100	100
Glycerine	25	..	..	25
Senegal-British gum thickening	..	635	585	..
Tragacanth thickening 6 per cent.	500	..	..	500
Tartaric acid	25	..	..	25
Water	50	..	..	50
Acetic acid tannin solution 50 per cent.	..	..	50	50
	1000 grms. each.			

These recipes are applicable to all Basic dyestuffs. After printing, steam and wash as usual. A run through a bath of tartar emetic may be given to goods printed according to recipes (III.) and (IV.). It increases the general fastness, but is not essential.

(c) Printing with Direct Colours.

The Direct dyestuffs, as a class, are well adapted to the printing of silk. They are less brilliant in shade but faster to water, washing, and perspiration than the ordinary Acid dyestuffs. In washing they are free from the defect of bleeding-out and leave the ground unstained. A great number of them are also of very good fastness to light—much superior in this respect to the Basic dyestuffs. A complete range of excellent printing colours may readily be selected from, amongst others, the following well-known series :—

Chlorazol Fast colours (I.C.I.).
Chlorantine Fast colours (S.C.I.B.).
Diphenyl Fast colours (Geigy).
Sirius colours (I.G.).
Chloramine Fast colours (Sandoz).
Diamine colours (I.G.).

These colours are usually printed in a slightly acid medium ; a few which are sensitive to acid are, however, printed in the same manner as for cotton, with an addition of the mildly alkaline sodium phosphate.

DIRECT DYESTUFF PRINTING COLOURS.

	I.	II.	III.
	grms.	grms.	grms.
Direct dyestuff	30	30	30
Glycerine	..	50	50
Water (hot)	670	360	300
British gum powder	250	..	..
Tragacanth mucilage 65 : 1000	..	..	550
Gum Senegal 1 : 1	..	250	..
British gum 1 : 1	..	250	..
Boil, cool, and add—			
Acetic acid 10° Tw.	50	60	..
Sodium phosphate (crystals)	..	..	20
Water	..	..	50
	1000 grms. each.		

Recipes (I.) and (II.) are suitable for the majority of Direct dyestuffs; (III.) is used for acid-sensitive colours, but may be used, if desired, for any Direct colour in place of (I.) or (II.). The presence of acetic acid is, however, of advantage where admissible.

Print, steam in cottage or continuous steamer for 1 hour, wash and dry.

(*d*) PRINTING WITH MORDANT COLOURS.

The Mordant dyestuffs are used in silk printing principally on account of their excellent all-round fastness, particularly to washing. The shades they give are not, in general, as brilliant as those obtained from Acid and Basic dyestuffs, and they have the drawback of "blinding" slightly, or detracting from the lustre of the silk fabric owing to the deposition of a relatively large amount of colour lake and insoluble metallic oxide on the fibre. On the other hand, they furnish an extensive range of fast colours, many of them of great depth and richness; they are applicable, in many cases without modification, to silk, cotton, and Viscose, and other regenerated cellulose artificial silks, and to materials consisting of mixtures of these fibres; and they are practically indispensable for the printing of dark blotches on the silk-faced cotton-backed satin so largely employed in the furnishing and bedspread trades.

Mordant colours of the Alizarin, Chrome, and vegetable groups in general are usually printed on pure silk with additions of 1 to 2 per cent. of either tartaric acid, oxalic acid or ammonium oxalate to the printing colours used for cotton. But these additions are by no means necessary as, in practice, cretonne patterns on silk-faced satin have been printed for years with Mordant and Basic colour printing pastes identical with those employed for cotton sateens; indeed the silk and cotton fabrics have been sewn end to end and printed, one after the other, without any change of colour, and without stopping the machine.

As mordants, the usual chromium acetate and aluminium sulphocyanide, etc., fulfil most requirements, but rather better results are obtained with the Acid Mordant dyestuffs (used only for pure silk or silk and wool mixtures) if chromium fluoride is employed as mordant.

The following recipes are typical of those in practical use:—

Alizarin Colours.

	I.	II.
Alizarin 20 per cent. paste	150 grms.	..
Alizarin bordeaux paste	..	100 grms.
Water	350 ,,	105 ,,
Glycerine	..	30 ,,
Acetic acid 9° Tw.	20 ,,	..
British gum powder	250 ,,	..
Gum tragacanth 50 : 1000	..	570 ,,
Lizarol D.	30 ,,	..
Oxalate of tin 25° Tw.	50 ,,	10 ,,
Acetate of lime 23° Tw.	35 ,,	50 ,,
Aluminium sulphocyanide 23° Tw.	100 ,,	70 ,,
Tartaric acid	5 ,,	..
Water	10 ,,	50 ,,
Ammonium oxalate	..	15 ,,
	1000 grms.	

In (I.), for reds and pinks, the Alizarin is boiled up with the water, acetic acid, and British gum, then cooled, and the other ingredients added cold. In (II.) the whole mixture is prepared in the cold.

Chrome Colours.

	I.	II.
Dyestuff in powder	25–50 grms.	50 grms.
Glycerine	30 ,,	20 ,,
Hot water	225–200 ,,	180 ,,
British gum thickening 1 : 1	600 ,,	..
Tragacanth thickening 50 : 1000	..	560 ,,
Acetic acid 40 per cent.	40 ,,	40 ,,
Chromium acetate 32° Tw.	80 ,,	150 ,,
	1000 grms.	

These recipes are suitable for colours of the type of Chromocitronines, Brilliant fast cyanine R., Gallazol green F.D., Alizarin yellows, Gallo navy blues, Modern blues and violets and, indeed, practically all ordinary Chrome mordant dyestuffs.

Acid Mordant Colours.

40 grms. Anthracene acid brown G. (I.G.).
30 ,, glycerine.
180 ,, water (boiling).
250 ,, British gum powder.
300 ,, water.

Boil, cool, and add—

25 grms. chromium fluoride
20 ,, ammonium oxalate } previously dissolved and cooled.
155 ,, water

1000

Silk goods printed with Mordant colours according to the foregoing general recipes, and also with vegetable dyestuffs, Logwood, Persian berries extract, etc., are steamed for an hour in the usual way, washed, soaped at 140° F. in the open width, washed again and dried. If the colouring includes Basic colours containing tannic acid, the goods are passed, immediately after steaming, through the customary fixing bath of tartar emetic and chalk before washing and soaping.

(*e*) Printing of Vat Colours on Silk.

The fact that silk is but little affected by moderate concentrations of alkali carbonates permits of its being printed with the majority of the Indigoid and Anthraquinone Vat dyestuffs. Even such dyestuffs of the latter group as require caustic soda for their effective reduction and initial solution may also be printed with safety provided that the caustic soda is subsequently converted into carbonate by the addition of a bicarbonate. In such cases it is advisable to provide against any excess whatsoever of caustic soda in the finished printing colour, for, although dilute caustic alkalies do not attack silk to any considerable extent *in the cold*, yet, under the conditions obtaining in steam agers, a very small excess is liable to tender the silk fibre, if not to destroy it altogether. In a less degree the same remarks apply to the effect of strong alkali carbonates; hence the necessity for cutting down the alkali content to a point as low as is consistent with the proper reduction of the dyestuff and the complete solution of the resulting leuco compound. Apart from the observance of these precautions, the printing of Vat colours on silk varies but little from the printing of the same colours on cotton.

The normal Rongalite-potash recipes, as used for cotton, may be adapted to silk simply by replacing any starch thickening which they may contain with British gum, gum Senegal, gum Arabic or other appropriate gum thickening. Printing colours based on these lines are prepared in several different ways, the choice of any one method being determined by the properties of the particular colouring matter employed or by the works' conditions under which it is to be applied.

Recipe I.

50–200	grms.	Vat dyestuff in paste.
700–650	,,	Potash thickening K. (below).
50–100	,,	Formosul or Rongalite C.
200– 50	,,	water or British gum thickening.
1000		

Heat to 140° F., cool, and allow to stand for 2–3 hours before use.

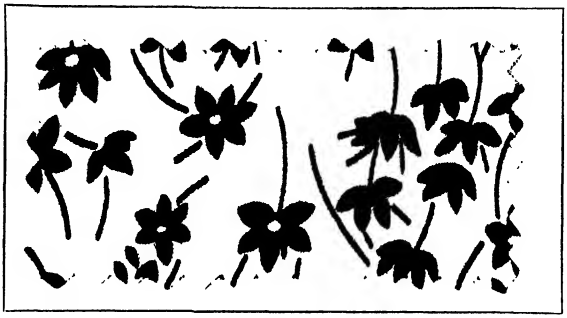
Potash Thickening K.

350	grms.	British gum.
400	,,	water.
100	,,	glycerine.
150	,,	potassium carbonate.
1000		

Heat until dissolved, then cool.

This recipe (I.) is suitable for Indigoid dyestuffs of the Ciba, Durindone, and Bromindigo groups. It may also be used for Anthraquinonoid dyestuffs

(Indanthrene, Caledon, Cibanone, etc.), in which case a better-yield of colour and more even prints are obtained by adding 5 to 8 per cent. of urea or 2½ per cent. of Dissolving Salt B. to the foregoing printing colours. The pattern below has been produced according to Recipe I.



Ciba Blue 2 B. dble. paste 100 grms. per Kilo. (S.C.I.B.).

CIBA BLUE.

100	grms.	Ciba blue 2 B. paste.
700	,,	Potash thickening K.
100	,,	Hydrosulphite R. conc. Ciba (or Formosul).
100	,,	water.
1000		

Print on unweighted silk. After printing the goods are steamed in air-free but not too dry steam for 5 minutes in the rapid ager, then passed through a warm reoxidising bath containing—

5	grms.	sodium perborate,
10	c.c.	acetic acid 40 per cent.,
1000	,,	water,

at 140° F., and finally washed in cold water, soaped at 160°–180° F., washed again thoroughly and dried, these operations being conducted in an open-soaping range.

RECIPE II.

100	grms.	Vat dyestuff, double paste.
50	,,	glycerine.
25	,,	Dissolving Salt B.
50	,,	water.
100	,,	potassium carbonate.
25	,,	hydrosulphite conc. ($Na_2S_2O_4$).
550	,,	British gum thickening.

Heat for ¼ hour at 120°–140° F., cool, and add—

100	grms.	Formosul or Rongalite C.
1000		

This recipe represents a general formula adaptable to all Vat dyestuffs used in silk printing. It may be varied as occasion dictates, the use of Dissolving

Salt B., for example, not being necessary for the majority of Indigoid dyestuffs. On the other hand its presence, or that of a little urea, is never detrimental and, in general, promotes fuller and more even shades.

Another useful method of preparing Vat printing colours for silk is based on the use of caustic soda in the first instance for reducing purposes, followed by an addition of sodium bicarbonate which, of course, converts the caustic soda into normal carbonate. It is applicable to all Vat dyestuffs, but is more particularly employed for those which are somewhat difficult to reduce completely in the absence of caustic alkali. It is also a useful method to adopt in the case of unusually strong or dark printing colours.

RECIPE III. (Bicarbonate Process).

100 grms. Vat dyestuff, double paste.
50 ,, glycerine.
50 ,, water.
50 ,, caustic soda 86° Tw.
30 ,, hydrosulphite conc. ($Na_2S_2O_4$).
550 ,, British gum thickening 1 : 1.

Heat to 120°–140° F., cool, and add—

60 grms. Formosul or Rongalite C.
60 ,, water.
42 ,, sodium bicarbonate.

Stir until dissolved.

Make up to 1000 grms.

Goods printed according to Recipes (II.) and (III.) are steamed and finished in exactly the same manner as indicated for Recipe (I.). If desired, the colours may be reoxidised after steaming, by a passage through a ½ per cent. solution (cold) of sodium bichromate instead of through perborate and acetic acid.

(*f*) INDIGOSOLS IN SILK PRINTING.

Vat dyestuffs in the form of Indigosols are readily printed on silk either by the steaming or certain wet-developing processes.

(*a*) STEAMING PROCESS.—This process is only suitable for pure, unweighted silk ; on tin-prepared or weighted material the colours are exceedingly liable to come out weak and irregular.

The printing colours employed are identical with those used for cotton but, after printing on silk, they require a much longer steaming for their proper fixation—a short ageing of 5–8 minutes, as given for cotton prints, is *not* sufficient to fix and develop them completely on the silk fibre. After printing, therefore, the silk goods are steamed for 30 minutes, then washed and soaped at 160°–180° F., washed again and dried.

Even at its best the steaming process does not give entire satisfaction in respect of colour yield, though useful for some styles. Much better results are obtained, in practice, from the wet-developing processes which are, moreover, applicable both to unweighted and tin-weighted goods.

(*b*) BICHROMATE PROCESS.—This process follows closely on the lines of the corresponding process used for cotton.

The printing colours are made up on the basis of the recipes tabulated below, and may be modified in detail according to the shades required.

PRINTING COLOURS.

	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol Yellow H.C.G.	60	..	..	..	..	..
,, Golden Yellow I.G.K.	..	40	..	..	..	..
,, Orange H.R.	..	..	60	..	..	..
,, Scarlet H.B.	..	..	..	40	..	..
,, Pink I.R. extra	..	..	..	..	30	..
,, Printing Purple I.R.	..	..	..	..	..	60
,, Developer G.A.	..	50	50	50	50	50
,, ,, D.	..	30	..	..	30	..
Glyecine A.	..	40	..	..	..	..
Solution salt B.	..	..	30	40	50	..
Dissolve in—						
Hot water	270	190	210	210	180	240
Natural gum	650	650	650	650	650	650
Sodium bichromate 1 per cent. sol.	..	..	..	10	10	..
Ammonia 25 per cent.	20	..	..	..	..	..
	1000 grms. each.					

	grms.	grms.	grms.	grms.	grms.	grms.	grms.
Indigosol A.Z.G.	50	..	..	..	..	..	..
,, O. 6 B.	..	50	..	..	..	..	..
,, O. 4 B.	..	..	50	..	..	..	..
,, Printing Blue I.G.G.	..	..	..	60	..	..	..
Indigosol Green I.B.	..	..	..	..	80	..	..
,, Brown I.R.R.D.	..	..	..	..	..	40	..
,, Printing Black I.B.	..	..	..	..	..	..	120
Indigosol Developer D.	..	..	..	..	..	50	..
Glyecine A.	..	..	..	30	50	..	..
Fibrit D.	..	..	..	..	..	50	..
Solution salt B.	..	..	..	..	..	50	..
Dissolve in—							
Hot water	300	300	300	260	200	200	230
Natural gum	650	650	650	650	650	600	650
Sodium bichromate 1 per cent. sol.	..	..	..	..	..	10	..
Ammonia 25 per cent.	..	..	..	..	20	..	..
	1000 grms. each.						

After printing, the goods are steamed for ½ hour, and the colours then developed by a treatment, in the rope form (or in a winch beck), for 5 minutes at 140° F. in a bath containing—

$$\begin{cases} \text{5 grms. bichromate of soda,} \\ \text{50 c.c. sulphuric acid 168° Tw.,} \\ \text{10 litres water,} \end{cases}$$

followed by a thorough washing, soaping at 160°–180° F., washing and drying.

(c) THE LEAD CHROMATE PROCESS and THE SODIUM CHLORATE PROCESS of printing Indigosols on wool are also applicable to silk printing. A full description of both processes will be found in the section on "Wool Printing."

(*g*) Aniline Black on Silk.

Aniline black still finds considerable use in the printing of silk, although it has, to a large extent, been replaced by the more convenient Neolan and Palatine Fast blacks, which may be printed along with any type of Acid colour and require no special after-treatment for their development.

Aniline Black I. (Standard).

100	grms.	wheat starch.
425	,,	water.
150	,,	tragacanth mucilage 6 per cent.
80	,,	British gum.
2	,,	Methyl violet (for sightening).
50	,,	sodium chlorate.

Boil, cool, and add—

100	grms.	aniline salt.
20	,,	aniline oil.

Stir until dissolved.

Make up to 950 grms.

For use	950	grms.	above standard.
	50	,,	copper sulphide 25 per cent. paste.
	1000		

Aniline Black II.

(A.)	120	grms.	aniline oil.
	5	,,	*p*-phenylenediamine.
			Heat to dissolve, cool, and add carefully—
	100	grms.	nitric acid 44° Tw.
(B.)	420	,,	starch-tragacanth paste.
	80	,,	red prussiate of potash.
(C.)	210	,,	starch-tragacanth paste.
	40	,,	sodium chlorate.
	25	,,	acetic acid 9° Tw.
	1000		

Mix (A.), (B.), and (C.) together just before use and when quite cold.

After printing and drying in hot air, the goods are aged for 4–5 minutes in the Mather-Platt rapid ager, chromed at 120° F. in a 1 per cent. solution of bichromate of soda, washed, soaped at 140° F., washed, and dried.

Black II. may be printed equally well on wool and wool and silk mixtures, and also on mixtures of these two fibres with cotton.

Discharge Styles on Silk.—The production of discharge (and resist) effects constitutes an important branch of the silk printing industry.

The majority of printed silk ties, mufflers, wraps, and handkerchiefs, and a large quantity of dress goods, are executed by one or other of these processes, and both lend themselves to a variety of styles.

As in wool printing both hydrosulphite and tin salt discharges are employed, according to circumstances. For machine printing the hydrosulphite discharges are by far the more convenient and, as they are applicable to a much wider range of ground shades than are the tin discharges, they are, to-day, almost universally employed for this class of work. On the other hand, the

tin discharges are still preferred for hand block printing on account of their greater resistance to air before steaming—a property of importance in the slow processes of printing by hand, since it allows of the printed goods being stored, for a day or two, until a sufficient quantity is ready for steaming in bulk.

(1) Hydrosulphite Discharges.

Ground shades for discharging are usually dyed on silk with Direct or Acid dyestuffs, the same dyestuffs being used as are employed for producing the corresponding discharge effects on wool fabrics. If anything, the Direct or Substantive dyestuffs are the more important on account of their superior fastness to washing and rubbing; but both classes are used largely for various styles of work, and the choice of a Direct or Acid colour is often merely a question of shade or convenience.

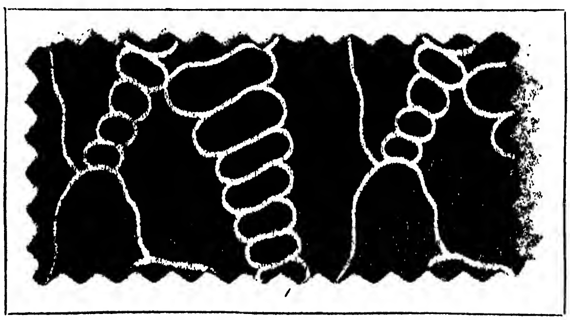
Direct or Substantive dyestuffs are dyed with an addition of acetic acid. The goods are first entered into a bath consisting of dyestuff solution *alone* and worked for 10–15 minutes at 85°–100° F.; acetic acid is then gradually added and the temperature raised during ½ hour to 180°–190° F., the dyeing being continued at this temperature for another ½ hour. The quantity of acetic acid employed varies from 5–10 per cent. on the weight of the silk, according to the particular dyestuff used and the depth of shade desired. After dyeing, the goods are washed thoroughly and dried—preferably on a stenter.

Acid dyestuffs are dyed similarly except that in the case of pure unweighted silk a more highly acidified dye bath is beneficial, *e.g.* 3 per cent. sulphuric acid, 168° Tw., and 3–5 per cent. Glauber's salt, calculated on the weight of the silk to be dyed. For tin-weighted silk it is not advisable to acidify the dye bath with sulphuric acid for obvious reasons. In its place an addition of 3–10 per cent. of acetic acid, or formic acid, provides the necessary acidity.

For dark grounds of good fastness to washing and "bleeding" any of the many Direct dyes that lend themselves to diazotisation and development on the fibre, or which couple with diazo solutions, are suitable provided that, at the same time, they remain dischargeable after these operations.

Suitable Direct and Acid dyestuffs for dischargeable grounds on silk will be found in the section dealing with "Discharge Styles on Wool." Any of the wool colours may be used for silk.

Of late years, a great advance in the fastness of silk discharge prints has been brought about by the introduction of the Neolan and Palatine Fast dyestuffs. These colouring matters, though belonging to the Acid group, are of remarkable fastness to light, soaping, washing in water and sea-water, and they

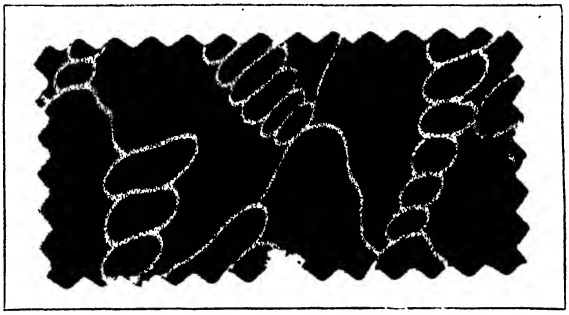


(S.C.I.B.)

5 per cent. Neolan Orange R. dyed on Unweighted Silk, and Discharged with Hydrosulphite R.W.S. Ciba.

are rapidly displacing the older dyestuffs in the production of the more exclusive high-class silk prints. They provide a complete range of full, rich shades, and although they are rather more difficult, and take longer, to dye than ordinary Acid and Direct dyestuffs, the results fully justify the extra trouble involved. They are readily discharged in white or colours by the usual hydrosulphite formulæ, and in this respect they present no difficulties and conform to current works' practice.

The dyeing of the silk material for the above and the following three patterns was carried out as follows:—The dye bath at 140° F. was set with 4 per cent. of acetic acid (40 per cent.) and the necessary percentage of previously dissolved dyestuff. The material was entered into the dye bath at this temperature and worked for ¼ hour. The temperature was then raised to 185°–195° F. and a further 2–4 per cent. of acetic acid added, according to the depth of shade required, and the dyeing continued at 190°–195° F. for a further 1½ hours. The goods were then thoroughly washed, and dried on a stenter (if possible) in readiness for printing with white or coloured discharges.



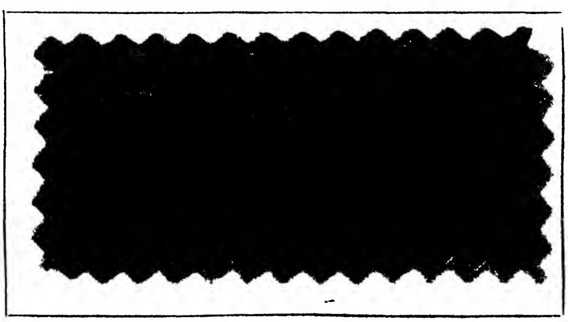
(S.C.I.B.)

5 per cent. Neolan Violet Brown B. on Unweighted Silk, Discharged with Hydrosulphite R.W.S. Ciba.

WHITE DISCHARGE.

250	grms.	Hydrosulphite R.W.S. Ciba.
50	,,	glycerine.
550	,,	British gum thickening 1 : 1.
150	,,	water.
1000		

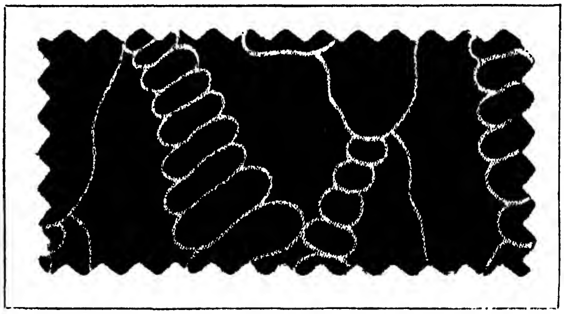
The printed and dried goods were steamed for 4–5 minutes in air-free steam in the rapid ager, then washed and dried.



(S.C.I.B.)

5 per cent. Neolan Navy Blue B. on Unweighted Silk, Discharged with Hydrosulphite R.W.S. Ciba.

On pure unweighted silk, good white discharges may equally well be obtained with ordinary hydrosulphite-formaldehyde compounds, such as Rongalite C., Formosul, Britulite, or Hydrosulphite R. conc. Ciba, but as a rule the brands containing zinc oxide or zinc carbonate are preferred, on account of their greater certainty of yielding clean white discharges.



(S.C.I.B.)

10 per cent. Neolan Black 2 R. on Unweighted Silk, Discharged with Hydrosulphite R.W.S. Ciba.

On tin-weighted silk the discharges are never quite so reliable as on unweighted material, owing to the tendency for the formation of coloured tin compounds (tin sulphides) during steaming. To avoid this disadvantage it is essential to steam the goods for as short a time, and at as low a temperature, as possible, and also to use only such hydrosulphites as contain zinc oxide or zinc carbonate, both of which prevent, or at least mask, the formation of tin sulphides. Zinc sulphide tends to be formed first, and as it is a white compound it has no harmful effect on the appearance of the discharges.

Amongst the hydrosulphite compounds used for discharges on weighted silk the following may be noted :—Formosul W., Rongalite C.W., and Hydrosulphite R.W.S. Ciba. If desired, zinc oxide or carbonate may be added to ordinary Formosul or Rongalite C. with quite satisfactory results. In the case of coloured discharges, mixtures of this kind are in general use and are more convenient than the special preparations of hydrosulphites.

The Palatine Fast dyestuffs are applied in the same manner as the Neolan dyestuffs and may be discharged according to the same methods or by the following recipe, which has given good results in practice :—

WHITE DISCHARGE (for Dark Shades).

200	grms.	Rongalite C.W.
100	„	water.
50	„	glycerine.
400	„	British gum 1 : 1.
50	„	Acetin N.
200	„	zinc carbonate 20 per cent. paste.
1000		

ZINC CARBONATE 20 PER CENT. PASTE.

900	grms.	zinc sulphate.
2000	„	hot water.

Add—

340 grms. soda-ash.
3000 „ water.

Boil, filter, wash the precipitate two or three times with water and allow it to drain, or press it, until it weighs 1950 grms.

After printing and drying gently the goods are steamed for 5 minutes in the rapid ager, washed and dried.

COLOURED DISCHARGES.—Coloured discharges on silk are produced principally by means of Basic and non-dischargeable Acid dyestuffs on grounds of Direct and Acid colours. A few Chrome mordant dyestuffs are also employed for colour discharges, and for special styles the Indigosols find occasional use.

As the same dyestuffs are used on silk as are used on wool—both for grounds and discharges—it is only necessary here to illustrate the preparation of typical printing colours together with a few notes on their general properties.

As regards fastness, the Basic dyestuffs are faster to washing than the Acid dyestuffs, but are much looser to rubbing and to light. Even an addition of tannin does little to improve their fastness to rubbing and "marking off"; but they are of extreme brightness, and this quality, together with their superior resistance to washing, renders them indispensable for discharge printing on silk. The range of "fast to rubbing" Acid colours is also very limited and must, of necessity, be supplemented by looser members of both the Basic and Acid dyestuff groups if variety of colouring and effect is to be obtained. Additions of Acetin, Phenol, Resorcin, Fibrit D., Glyecine A. or Aniline oil to Basic colour discharges all retard the formation of the tannin-lake and, in this way, they help considerably to improve the fastness to rubbing, especially if excess of dyestuff is avoided in the first instance and if the goods are fixed in tartar emetic and thoroughly well washed after steaming. Fixing in tartar emetic is, however, rarely resorted to in practice.

BASIC COLOUR DISCHARGES ON SILK.

	I.	II.	III.	IV.
	grms.	grms.	grms.	grms.
Basic dyestuff	30	30	30	30
Resorcin	50	..	..	..
Acetin	30	50	..	..
Glyecine A. (or Fibrit D.)	..	..	30	..
Methylated spirit	..	50	50	50
Water	200	205	220	270
Gum thickening 1 : 1	500	475	480	500
Formosul or Rongalite C. 1 : 1	100	100	100	100
Tannin-alcohol 1 : 1	40	40	40	..
Zinc carbonate 20 per cent. paste	25	25	25	25
Gum thickening 1 : 1	25	25	25	25
	1000 grms. each.			

The solution of tannic acid in alcohol may be omitted. Basic colours fix on silk without tannin and are fairly fast to washing, but the presence of tannin improves the resistance of the colour to washing and rubbing, and is usually preferred for the best work.

ACID COLOUR DISCHARGES ON SILK.

	I.	II.	III.
	grms.	grms.	grms.
Dyestuff	30	30	30
Acetin	..	50	..
Fibrit D.	35	..	..
Methylated spirit	60	..	70
Resorcin	..	50	..
Water	245	240	270
Senegal gum 1 : 1	480	480	480
Rongalite C. 1 : 1	100	100	100
Zinc carbonate 20 per cent. paste	25	25	25
Gum solution 1 : 1	25	25	25
	1000 grms. each.		

These two groups of Basic and Acid colour recipes are suitable for printing on either weighted or unweighted silk. Appropriate dyestuffs will be found in the lists given for discharges on wool.

CHROME (MORDANT) COLOUR DISCHARGES.

30	grms.	Chrome colour in powder.
30	,,	Fibrit D.
240–220	,,	water.
500	,,	British gum 1 : 1.
80–100	,,	Formosul or Rongalite C.
120	,,	chromium acetate 30° Tw.
1000		

For the printing of black outlines or "boundages" around hydrosulphite discharges where the contours of the latter fit tightly up against the black, it is necessary to employ dyestuffs which are resistant to the destructive action of hydrosulphites. The following two blacks fulfil this condition and will serve as guides to the preparation of similar outline colours.

OUTLINE BLACK I. (I.G.).

60	grms.	Fast blue O.
1	,,	Sulphorhodamine B.
9	,,	Quinoline yellow ex. conc.
30	,,	Fibrit D.
250	,,	water.
570	,,	tragacanth mucilage 60 : 1000.
20	,,	oxalic acid.
10	,,	aluminium sulphate.
50	,,	water.
1000		

Outline Black II.

60	grms.	Modern heliotrope D.H.
15	,,	Flavophosphine 4 G. conc.
20	,,	formic acid 90 per cent.
40	,,	acetic acid 9° Tw.
215	,,	water (boiling).
500	,,	British gum 1 : 1.

Dissolve by heat, cool, and add—

150 grms. tannin-acetic solution 1 : 1.

1000

After printing with the discharge colours, the silk goods are carefully but thoroughly dried and then steamed for 4–5 minutes in damp, air-free steam in the rapid ager at 212°–216° F. They are then wound between *dry* greys, in the usual manner, and re-steamed, without pressure, for ½ hour in the cottage steamer for the purpose of effecting a more complete fixation of the discharge colours. Where time and accommodation are available, it is of advantage to hang the printed pieces for 24 hours between the first and second steamings in order to allow such discharge colours as Thionine blue, Methylene blue, Nigrosines and some Eosines and Rhodamines to re-oxidise gently in air. In any case, after the second steaming, the goods are passed through a bath of bichromate of soda (1 grm. per litre), well washed, soured in acetic acid, washed and dried.

For very dark ground shades and for diazotised and developed dyeings the quantity of sulphoxylate-formaldehyde (Rongalite C., etc.) may be increased as required, and in the case of heavily weighted silk the content of zinc carbonate, 20 or 25 per cent. paste, may be increased to 150 grms. per kilo. of discharge printing colour, especially for white discharges.

(2) Tin Discharges on Silk.

In machine printing from engraved rollers, tin discharges on silk have been displaced almost entirely by the more comprehensive hydrosulphite discharges which, in general, yield better results and are more reliable in action. For hand block printing, which is a slow process, the tin discharges, however, are still of importance because, as already noted, they permit of a longer interval between the operations of printing and steaming.

White discharges, though produced, are not pure and are never satisfactory, and they are rarely employed. Tin salts form difficultly soluble compounds on silk in steaming—compounds which cannot be removed entirely even by souring with mineral acids—with the result that, after a time, the discharged portions turn yellow or take on a brownish tinge.

The tin discharges given for wool (*q.v.*) are equally suitable for silk, and the same dyestuffs are employed. It is to be noted that tin discharges with Basic dyestuffs are faster to rubbing than the corresponding colours in hydrosulphite discharges—a property of considerable practical interest.

Stannous chloride (" tin salt ") and stannous acetate are both used as discharging agents. Stannous acetate is often preferred because it allows of a full hour's steaming, whereas stannous chloride discharges act more energetically on the silk fibre and must not be steamed for more than 10–15 minutes and without pressure. The longer steaming gives a better fixation of the colouring matter, and is also easier to regulate.

The grounds are preferably dyed with Direct dyestuffs which are, in the

main, faster to washing than Acid dyestuffs and, as a rule, more readily discharged by stannous salts.

The application of tin discharges to silk is practically restricted to block-printing on *unweighted* material, and the formulæ given below refer to this class of work.

Recipes embodying stannous chloride are not described here since those indicated for wool will serve as types for silk.

Stannous acetate discharges are made up on the basis of the following:—

STANNOUS ACETATE DISCHARGES ON UNWEIGHTED SILK.

	Basic Colour.	Acid Colour.
Basic dyestuff	30 grms.	..
Acid dyestuff	..	30 grms.
Acetin	30 ,,	30 ,,
Citric acid	30 ,,	30 ,,
Water	110 ,,	110 ,,
Senegal gum 1 : 1	200 ,,	200 ,,
Discharge paste (below) S.A.	600 ,,	600 ,,
	1000	1000

DISCHARGE PASTE S.A.

1000 c.c. stannous acetate 29° Tw.
250 grms. British gum powder.

1250 grms.

Warm to dissolve the gum and cool before use.

STANNOUS ACETATE 29° Tw.

I. 3100 grms. lead acetate (sugar of lead).
2000 c.c. water.
300 ,, acetic acid 9° Tw.

Dissolve and add—

II. 2000 grms. stannous chloride.
1000 c.c. water.

Allow the mixture of (I.) and (II.) to settle; filter off the precipitate of lead chloride and set the filtrate of stannous acetate at 29° Tw. The stannous acetate so obtained contains a small proportion of stannous chloride, which increases its activity and is an advantage.

Discharges containing Eosine dyestuffs, *e.g.* Phloxine, Erythrosine, Rhodamine, etc., are improved by an extra addition of 20 grms. or more citric acid per kilo. of printing colour.

STEAMING.—The dyed silk goods, printed with *stannous acetate* discharges, are gently dried, wound in dry greys and steamed for 1 hour in a cottage steamer without pressure. They are then well washed, soured in acetic acid, washed, and dried. They may also be steamed, between greys, in the continuous steamer if a cottage steamer is not available, but the results are apt to be irregular.

Stannous chloride discharges are steamed without pressure for 10–15 minutes only, in a cottage steamer, and thereafter washed, soured in acetic acid, washed, and dried in the usual manner.

(3) Indigosol Discharges on Silk.

This interesting but hitherto little used process for obtaining *fast* coloured discharges on dyed silk piece goods is based on the fact that Indigosols are not destroyed by hydrosulphites but merely prevented temporarily from developing and may, subsequently, be fully re-oxidised and developed on the fibre by a passage through a warm bath of dilute nitrous acid.

The principle of the process consists in adding Formosul or Rongalite C. to the ordinary Indigosol (or Soledon) printing colours and steaming in the rapid ager for about 8 minutes as usual for such colours. In this way the Indigosols and Soledons are fixed on the fibre and, simultaneously, the dyed ground shade is discharged on the printed parts. The fixed, but undeveloped, Indigosol colours are then fully re-oxidised and developed by passing the goods through a bath of nitrite of soda and sulphuric acid followed, after thorough washing, by a light soaping.

The process is somewhat limited, for the reason that only such dyestuffs as will withstand the action of nitrous acid are available for dyeing the ground shades. The following Acid and Direct dyestuffs fulfil this condition, as they are either only very slightly affected by the developing bath or withstand it completely:—

Direct Dyestuffs.

Benzo fast orange S.	Toluylene fast orange G.L.
Benzo fast scarlet B.B.S.	Diamine pink F.F.B.
Sirius red 4 B.	Benzo violet R.
Sirius blue 6 G.	Benzo azurine G.
Benzo new blue B.B.	Solamine green B.
Diamine green B.	Diamine brown M.
Sirius grey G.	Diazo fast black S.D.

Diazo brilliant scarlet B.G. extra, diazotised and developed with β-naphthol.
Diazo brilliant scarlet R.O.R., ,, ,, ,,
Diazo light red 7 B.L., ,, ,, ,,
Diazo bordeaux 29500, ,, ,, ,,
Diazo indigo blue 3 R.L., ,, ,, ,,
Diazo light yellow G.G., diazotised and developed with phenylmethylpyrazolone.
Diazo brilliant scarlet R.O.R., diazotised and developed with phenylmethylpyrazolone.
Diazo light green G.F.L., diazotised and developed with phenylmethylpyrazolone.
Diazo fast black S.D., diazotised and developed with phenylmethylpyrazolone.

Acid Dyestuffs.

Wool orange G.N.	Fast red A.
Supramine red G.G.	Supramine red B.
Brilliant wool blue F.F.R. ex.	Alkali fast green 10 G.
Naphthylamine black 4 B.L.	

These dyestuffs are all manufactured by the I. G. Farbenindustrie A.G., but similar ranges may be compiled from the lists of English and Swiss dyestuff makers.

The silk goods dyed with any of the foregoing dyestuffs are printed with—

INDIGOSOL DISCHARGE COLOURS.

	1.	2.	3.	4.	5.
	grms.	grms.	grms.	grms.	grms.
Indigosol Printing Blue I.G.G.	60	..	..	..	..
„ Green I.B.	..	80	..	..	..
„ Golden Yellow I.G.K.	..	..	50	..	..
„ Pink I.R. Extra	..	..	..	40	..
„ Scarlet H.B.	..	..	..	..	50
Glyecine A. or Fibrit D.	30	30	30	50	50
Water	258	238	268	258	248
Natural gum	550	550	550	550	550
Rongalite C.	100	100	100	100	100
Soda-ash	2	2	2	2	2
	1000 grms. each.				

After printing and drying, steam for 8 minutes in the rapid ager or other apparatus, *wash* in water in the open width, pass for 8 seconds at 65° C. through a bath of—

2 grms. sodium nitrite,
20 c.c. sulphuric acid 168° Tw.,
1000 „ water,

wash thoroughly, soap lightly if necessary, wash, and dry.

Indigosol pink I.R. (No. 4 above) gives a bright pink discharge which is quite fast to rubbing.

Resist Styles on Silk.—For these styles stannous chloride, hydrosulphite, and resin, fat, and wax resists are used; the two first mainly for resists under cover prints, the last for resists under dyed grounds.

The tin and hydrosulphite resists are made up like discharges, with sometimes an addition of zinc oxide or China clay, and are printed on white silk, which is afterwards covered with another pattern in Acid or Direct colours. The goods are then steamed and washed as usual.

Resin, fat, and wax resists are printed hot, as when cold they set hard. Either block or roller machine may be used, and there is no reason why stencilling should not be employed for certain styles. Coloured resists with resin, etc., are obtained by first printing in the colours by block, and then, after drying, printing the whole pattern again with the same set or a similar set of blocks in the resisting mixture. In this way any desired colours may be *reserved* during the subsequent dyeing of the ground shade; and as the resists act in a purely mechanical manner, the dyed shade and the reserved colours need not be specially selected for their respective dischargeable and resisting properties. Hence any silk colour is equally applicable to either the reserved pattern or the dyed ground.

The resin mixtures are known as Mastic Resists. The following two recipes will illustrate the composition of these mixtures:—

MASTIC RESISTS.	I.	II.
Resin	600	300
Beeswax	100	60
Swedish Pitch	..	100
Stearin	..	40
Benzene or Petrol	300	..
Naphtha	..	500
	1000	1000

After printing the resists are dusted with talc powder or French chalk to prevent them from marking off or sticking together, and the goods are then dyed in the cold. When sufficiently dyed, the wax and resin are removed by working the silk in a bath of benzene or naphtha, neither of which dissolves the colours.

For the production by the Mastic Process of a so-called bandana handkerchief in red, yellow, blue, and white on a dark green ground the following sequence of operations may be carried out:—(1) Block print the white silk with thickened pastes of Victoria scarlet, Victoria yellow, Cyanol extra. (2) Steam for $\frac{1}{2}$–1 hour without pressure. (3) Wash and dry to width on a stenter. (4) Print the mastic reserve over the previously printed red, yellow, and blue, and on the parts of the silk cloth where the white, omitted in the first printing, is to appear. (5) Dye in the cold, or at 20°–25° C., in the following:—

2 per cent. Methylene green.
$\frac{3}{4}$ per cent. Auramine O.
10 per cent. acetic acid.
10 per cent. Glauber salt.

Work in the dye liquor until the required depth of shade is obtained, rinse in water, hydro-extract, hang up to dry, and (6) Wash in benzene or carbon tetrachloride until the mastic reserve is entirely removed. After the solvent has evaporated from the goods, the fastness of the ground shade may be increased by a second steaming for $\frac{1}{2}$ hour, but this is rarely necessary. Instead of the colours used above, any others suitable for silk may be employed in like manner.

Printing of Satins and Half-Silk.

The printing of satin goods is carried out in exactly the same manner as that of cotton goods, so that, with the exception of certain Vat dyestuffs, the Azoic colours in general and Madder dyed colours, all the colouring matters used for cotton may be employed in precisely the same way for half-silk goods containing cotton. The presence of the latter requires the addition of tannin and chromium acetate to Basic and Eosin colours respectively, otherwise they would wash out at once in the first wash.

On account of the silk contained in the fabric, the Azoic colours—Paranitraniline red, etc.—are unsuitable for satin, as they cannot be obtained free from the defect of rubbing off.

The Aniline black given for silk is equally adaptable to satin, and Paramine brown also serves as a suitable ground and outline colour.

The colours used in the direct printing of satin being for the most part fast, will stand soaping, and can therefore be thickened sometimes with starch ; as a rule, however, it is better to use gum Senegal, gum tragacanth, or British gum, since they wash out very easily, leaving the lustre of the silk unimpaired.

Starch may be employed for dark outlines, but for blotches and other masses of colour, whether dark or light, the gums give by far the best results, especially in the case of fabrics one side of which is almost pure silk, such as the furniture satins with a cotton back and silk face.

Apart from furniture cretonne patterns, the most important branch of half-silk printing is that connected with discharge and resist styles.

Aniline black and Paramine brown discharge styles are carried out exactly as described for cotton.

The Browning process, as might be expected, gives the most lustrous, if not

the brightest, colours on Aniline black, and is perhaps, on the whole, the most suitable, but other processes give satisfactory results, and even the presence of zinc oxide (Kay's process) is unobjectionable in fine discharge patterns, which, while they lose somewhat in lustre, gain more in brilliancy of colour.

The purest whites are obtained by the resist-method, especially those produced under Nitroso-blue, in what is known as the Foulard Blue Style.

The application of Nitroso-blue to half-silk is similar to its application to cotton, but both printing and slop-padding colours require an increased quantity of acid to yield the best results.

The following process for producing white resists under Nitroso-blue has been used successfully on the large scale:—The goods printed with the resist paste are thoroughly dried, then padded in Nitroso-blue M.R., and finally steamed, fixed in tartar emetic, washed, soaped, washed, and dried.

WHITE RESIST.

170	grms.	British gum.
195	,,	water.
130	,,	glue solution 1 : 2.
85	,,	acetic acid 12° Tw.
250	,,	stannous chloride.
170	,,	tartaric acid.
1000		

Print, dry, and pad the goods in—

BLUE M.R.

	I.	II.
	grms.	grms.
Nitroso-base M. 50 per cent.	50	50
Hydrochloric acid 36° Tw.	16·7	16·7
Water	140	170
Tannoxyphenol R.	..	63
Resorcin	33	..
Hot water	85	85
Tannin solution 50 per cent.	100	..
Oxalic acid 10 per cent.	420	420
6 per cent. tragacanth thickening	100	100
Make up with water to	1000	1000

Pad, dry carefully in hot air, steam at 100° C. without pressure for 5–15 minutes, pass through a 1 per cent. solution of tartar emetic, wash, soap, wash, and dry as usual.

The same process may be applied to pure silk.

PART XI.

THE PRINTING OF ARTIFICIAL SILKS.

THE PRINTING OF ARTIFICIAL SILKS.

DURING the last twelve years the printing of artificial silks has developed into an increasingly important branch of the textile industry and, already, printed fabrics of this description have, to a great extent, taken the place of many of the finer quality of older cotton prints.

Unlike artificial alizarin and indigo, which are identical in chemical composition and properties with the *pure* natural products, artificial silks do *not* consist of real silk manufactured synthetically. Apart from their lustre, and perhaps their microscopic appearance, they bear no resemblance to genuine silk either in physical properties or in chemical structure; they are, in fact, only imitation silks, and to describe them as *silks* is really to misrepresent their nature and value. The trade has recognised this misdescription and, commercially, all imitation silks are now designated "Rayons." The term "artificial silk" is, however, still in popular use throughout the world and must, in consequence, be tolerated until it is finally superseded by the more distinctive appellation *Rayon.*

It is unnecessary here to discuss the chemical technology of the various rayons, which may be found fully described in the many works devoted specially to the subject of textile fibres.[1] From the textile printing and dyeing point of view the commercial rayons may be divided into two main groups:

(1) Regenerated cellulose rayons, as exemplified by:

- (*a*) Cellulose nitrate or Chardonnet silk.
- (*b*) Cuprammonium: Glanzstoff and Pauly silk.
- (*c*) Viscose rayon.

(2) Cellulose acetate rayon, of which the best known example is "Celanese."

These two groups are each characterised by distinctive chemical properties, and they differ so fundamentally in their behaviour towards dyestuffs that they can be dealt with only under separate headings.

(I.) REGENERATED CELLULOSE RAYONS.

Members of this group, of which Viscose is the most important, consist of practically pure cellulose and, in consequence, they possess an affinity for all types of dyestuffs which are applicable to cotton. Hence all styles and colouring matters used for cotton printing are equally suitable for rayons of this group, except such styles as require prolonged and vigorous treatment in dye baths and soaping ranges, as, for example, the Madder and other dyed styles on previously applied metallic mordants. As a rule regenerated cellulose rayons are of a fragile nature, especially when wet, and all processes which involve heavy after-treatments in the rope form in spiral washing, dyeing, and soaping machines must be avoided as much as possible. If, at times,

[1] For a concise and lucid description of the subject see *The Bleaching, Dyeing and Chemical Technology of Textile Fibres*, by S. R. and E. R. Trotman (Charles Griffin & Co., Ltd.), also *Artificial Silks*, by the same authors and publishers.

operations in the rope form are necessary, it is advisable to carry them out in elliptical winch machines or in rope becks constructed on the principle of slack washing machines.

As all regenerated cellulose rayons, by whatever process they are manufactured, consist finally of pure cellulose, they will be dealt with collectively in the following pages under the name of "Viscose." It is true that nitro-cellulose, or Chardonnet rayon, differs slightly from the others of its group in having a direct affinity for Basic dyestuffs, but this property calls for no variation in printing practice and is of little importance, since almost all rayon printing cloths are unions or mixtures of cotton and Viscose or other similar rayon fibres, and all are printed by methods identical with those used for cotton alone.

Scouring and Bleaching of Viscose Rayon Fabrics.

(*a*) Viscose-cotton goods containing cotton which has not previously been kier-boiled may, with care, be kier-boiled and bleached in the usual manner with bleaching powder or, better, with sodium hypochlorite, which leaves the cloth with a softer feel than bleaching powder. Viscose is easily over-oxidised to oxycellulose, and care must be taken to avoid the use of too highly concentrated bleaching liquors. A concentration of $\frac{1}{2}°$ Tw. sodium hypochlorite is ample as a maximum in most cases, and frequently much weaker liquors are efficient if the goods are allowed to lie in pile before souring and washing. After treatment in hypochlorites, the goods are washed, soured in sulphuric or hydrochloric acid at $\frac{1}{2}°$–1° Tw., and again thoroughly well washed to remove every trace of acid. They are then hydro-extracted and dried. Needless to say, all operations are carried out on machines which impose as little strain on the cloth as possible. Kier boiling and bleaching in this way demand the utmost care at every stage in order to avoid chemical attack on, and mechanical injury to, the viscose fibre.

(*b*) An alternative method is to discard kier boiling in favour of a scour in an alkaline soap bath, after which the goods are bleached in sodium hypochlorite as before. Bleached by this method, however, the cotton content of the material, although bleached to a good white at first, has a tendency to turn yellow when steamed or stored for any length of time.

(*c*) A better and more reliable method of obtaining an excellent and permanent white on viscose-cotton unions consists in treating the soap-scoured goods in moderately hot, slightly *alkaline* solutions of hydrogen peroxide. Acid and neutral solutions of hydrogen peroxide exercise very little bleaching action on cotton at practicable concentrations and, moreover, they tender the fibre; but if rendered slightly alkaline, the peroxide bleaches efficiently and leaves the fibre very little impaired—certainly not beyond permissible limits, and less than when hypochlorites are used as bleaching agents. On the other hand, excess of alkali over the minimum required for a good bleach serves no useful purpose; it increases the rate of evolution of oxygen from the hydrogen peroxide and thus causes the solution to decompose rapidly and become useless before the bleaching is complete, and, at the same time, it causes increased tendering of the fibre. Too high a temperature in bleaching also causes an increase in the chemical attack on the goods, though not always to a prohibitive extent unless continued for too long.

Various substances may be added to the solution of hydrogen peroxide to produce the necessary alkalinity in the bleaching bath, *e.g.* ammonia, sodium phosphate, caustic soda, silicate of soda and other, little used, salts. Of these, silicate of soda is usually preferred and it gives eminently satisfactory results when at a suitable concentration and temperature.

A process which has given good results in practice is worked as follows:—

(I.) Scour the goods in a winch beck for 2 hours at the boil in a soap bath containing—

$$\left.\begin{cases} 1500 & \text{litres water.} \\ 5{\cdot}2 & ,, \quad \text{caustic soda } 88^\circ \text{ Tw.} \\ 3 & \text{kilos. soap.} \end{cases}\right\} \text{at } 212^\circ \text{ F.}$$

(II.) Wash well and for about 50 kilos. of cloth bleach in a bath of—

$$\begin{cases} 1000 & \text{litres water.} \\ 10 & ,, \quad \text{silicate of soda } 100^\circ \text{ Tw.} \\ 20 & ,, \quad \text{hydrogen peroxide 100 vols.} \end{cases}$$

Work the goods in this bath for 1 hour at 175°–180° F. (79°–82° C.), wash well, sour if necessary, hydro-extract, and dry. If the goods are to be dyed with Direct colours for discharge styles, souring may be omitted, but for steam styles the presence of traces of free alkali is usually detrimental and they must, therefore, be removed by a light souring in any acid.

Direct Printing of Viscose Fabrics.

The preparation of printing colours for this purpose is the same as for cotton, except that only easily soluble thickenings may be used. Starch thickenings may be employed for printing very small objects and for fine line work, but for general work they must be avoided. They fill up the interstices of the cloth and adhere so tenaciously to the fibres that only an energetic washing and soaping, after steaming, will remove them. Rayon fabrics in the wet state are too fragile to withstand such drastic treatment and, therefore, it is essential to use gum thickenings which wash out from the cloth easily in open width machines. The principal thickening materials employed are the natural gums—Senegal, Arabic, and Tragacanth—and British gums, all of which are readily removed from the fibre in an open soaping range of the usual type.

In their affinity for dyestuffs, viscose and other regenerated cellulose rayons approximate closely to ordinary cotton, and for all practical purposes they may be treated as cotton, keeping in mind always their more delicate nature. Apart from the mordant-dyed styles—*e.g.* Turkey red and Madder reds, purples, chocolates, etc.—all dyestuffs, processes, and styles that are applicable to cotton are, in like manner, applicable to viscose rayon and its combinations with cotton. If desired, viscose fabrics and pure cotton materials may even be printed together, in many instances, without change of colour, provided that no starch thickenings are employed for the solid parts of the pattern.

This similarity in behaviour towards dyestuffs renders it unnecessary to give detailed recipes for the making-up of printing colours. There are, however, one or two points in connection with the use of certain types of colouring matters which call for attention, and, therefore, for the sake of completeness, a brief recapitulation is given below of the general principles underlying the application of the several groups of dyestuffs appropriate to the printing of viscose rayons.

The **Basic colours,** thickened with gums and using tannic acid as fixing agent, are applied in a manner identical with that employed for cotton. If British gum is used for thickening, it is advisable to select a light-coloured, soluble quality, as free as possible from unconverted starch.

Mordant colours of all descriptions, viz. Alizarin, Chrome mordant, and vegetable dyestuffs, are all printed according to the various methods in use

for cotton. With regard to thickenings, it is to be noted that certain qualities of Senegal and Arabic gums are coagulated, during steaming, in the presence of metallic mordants (particularly sulphate-acetates of chromium) and thus, being converted into insoluble compounds which cannot be removed by washing and soaping, they impart an undesirable permanent hardness to the goods. Not all qualities behave in this manner, but when the difficulty does arise it may sometimes be overcome by the use of a *pure* chromium acetate or, better, obviated altogether by the employment of a British gum thickening.

Vat colours are usually printed on viscose rayons by the Rongalite-potash process, but any of the many formulæ in use for cotton are also applicable. In the after-treatment care must be taken to avoid undue strain on the cloth, and to this end all operations of oxidising, washing, and soaping are best carried out in the open width and at a temperature not exceeding 80° C. (175° F.). In the case of **Sulphur colours**, any type of recipe suitable for a given dyestuff may be employed, the after-treatment being the same as for Vat colours. The Sulphur colours, however, find very little outlet in the printing of rayons.

The **Azoic colours** of the Naphthol A.S. and Brenthol A.S. series are of great importance in all branches of viscose rayon printing. They may be used in direct, discharge and resist printing on all types of regenerated cellulose rayons and on mixtures of these fibres with cotton in the same manner as on all-cotton goods. It must be noted, however, that viscose and similar synthetic fibres are less absorbent than cotton, *i.e.* they wet-out much less readily, particularly in the cold. At higher temperatures the difference is almost unnoticeable; hence viscose-cotton goods impregnated with Naphthols or Brenthols of the A.S. range are preferably padded at a fairly high temperature, viz. 140° to 175° F., in order to increase the receptivity of the viscose content for the dyestuff produced on the fibre by coupling with diazo solutions. Incidentally this high padding temperature not only gives more even shades, due to more or less equal absorption of the padding liquor by the two constituent fibres of the material, but also minimises the difficulties that arise out of the high substantivity (affinity for the fibre) possessed by many of the A.S. Naphthols. In regard to after-treatment, washing and soaping should not be conducted at temperatures exceeding 175°–190° F. The hotter treatment is confined to colours which require a hot soaping to bring about the full development of shade, *e.g.* the combinations Naphthol A.S.-B.G./ Fast scarlet salt G.G., Naphthol A.S./Fast violet base B.B., pink shades of Naphthol A.S.-R.L./ Fast red R.L. base, and several other combinations.

The Rapid Fast, Rapidogen, and Rapidazol colours are applied to viscose rayons by the normal methods in use for cotton printing, and no special complications present themselves.

The **Indigosol and Soledon dyestuffs** are of increasing importance in the production of fast prints on the better qualities of viscose rayon fabrics. Their application differs in no wise from that to cotton and calls for no special mention, since all the various steaming and developing processes are common both to viscose and cotton.

Direct cotton colours are principally used for the dyed ground shades of discharge styles. To a limited extent they are also used in printing in cases where no great fastness to washing is demanded. Solutions of the dyestuff in water, glycerine, and sodium phosphate are thickened with British gum or tragacanth and printed, steamed, and washed exactly as for cotton. Steaming in moist steam without pressure gives the best results and yields shades which are bright and somewhat faster on viscose than on cotton.

Aniline black and other oxidation colours are printed by any of the recipes already given for cotton, and require no more than the usual care.

Steaming of Viscose Rayons.

Steaming and ageing operations connected with the printing of all kinds of rayon fabrics are carried out in the usual rapid agers and continuous steamers, and no special precautions are necessary beyond the avoidance of undue strain in the mechanical handling of the goods. In view of the fact that viscose and other regenerated cellulose rayons are more sensitive than cotton, and that they are very liable to fray and break under conditions of handling that would leave cotton goods unaffected, it is essential to provide easy-running plant for their mechanical treatment and to see that all tension and guide rails are smooth, and, if of wood, that they are free from outstanding knots due to uneven wear. In this way excessive pull, friction, strains, and stresses will be avoided. The best results in steaming are obtained in modern plant such, for example, as the Mather & Platt and John Wood continuous automatic steaming and ageing machines in which the goods, hanging in loops free from strain, may be steamed for varying periods from 7 minutes to an hour. Similarly, for goods which require only a short ageing—discharge and resist styles, Vat colours, Aniline blacks, etc.—the modern combined hydrosulphite and aniline ageing machines are superior to older types in that most, and in some cases all, of the top row of guide rollers are driven through bevel or mitre wheels and thus relieve the travelling cloth of the strain of pulling them round, as was necessary in earlier agers. Occasionally, too, for special purposes or unusually delicate fabrics, the bottom guide rollers are also driven, and not infrequently both top and bottom rollers are fitted with ball bearings in order to eliminate all tension on the cloth. Cottage steaming is rarely employed for viscose goods and is never, at any time, necessary.

After-treatment of Viscose Rayons.

As no mordant-dyed styles are produced on viscose rayons the after-treatment of steamed goods is confined to processes of fixing, chroming, washing, and soaping, all of which are preferably carried out, in the open width, on machines of the open soaping type. Elliptical winch washing machines (fig. 71) are also used for washing purposes and for soaping Vat colour prints with advantage, but for general work, on anything but the most delicate fabrics, an open soaping machine fulfils all requirements. If, from any cause, neither of these machines is available, it is possible to treat viscose goods in ordinary spiral washing and soaping becks; all that is required is to lift the upper of the two squeezing bowls out of contact with the lower and carefully prevent the goods from running tight or getting entangled in the bottom of the beck, or "ballooning." These difficulties are liable to arise with light, thin materials, and they usually result in frayed or torn cloth.

An improved method of washing every kind of rayon fabric, without the slightest tension or strain on either the warp or weft threads, is embodied in the "Ripple" washing machine of Messrs Mather & Platt, Ltd. In this machine the cloth is delivered, in the open width, to an inclined plane of plate glass, down which it is washed gently by sprays of water to a horizontal travelling apron or "creeper" of phosphor bronze wire gauze. The cloth slips down freely from the glass plane to the travelling apron and, owing to the relative speeds of cloth and apron being 3 : 1, the cloth is delivered to the apron three times as quickly as the apron carries it forward. This results in the cloth being formed into small folds or "ripples" on the apron, which is thus enabled to carry a length of cloth three times greater than its own working

length. The travelling cloth is washed by sprays of water delivered by spirt pipes working on the counter-current system. The spirt pipes are arranged in three sets along the machine; clean water is supplied to the last set at the exit end and, after washing the cloth, passes through it into a cistern beneath, from which it is pumped through the second set of pipes, and again, after washing and passing through the cloth, similarly pumped through the first set at the entering end of the machine. The machine can be arranged for washing with hot water, or for soaping, if desired. When used for rayon fabrics it is frequently modified so that one half is utilised for soaping and the other half for washing, thus taking the place of an open soaping range without imposing the latter's longitudinal pull on the warp of the cloth.

The drying of viscose rayons presents no complications and may be conducted on any ordinary cylinder machine.

Discharge Styles on Viscose Rayons.

In all probability there are more viscose rayon fabrics printed by discharging processes than by any other means. The discharge style is of importance in this branch of printing (as also in others) because, apart from eliminating the cost of engraving blotch rollers, dyed ground colours are distinguished by greater fullness, richness, and liveliness of shade than those produced by blotch printing and, moreover, they leave the cloth with a softer feel and unimpaired lustre. Further, finely engraved patterns, consisting of delicate lines, small spots, circles, and other *motifs*, which would be swamped in blotch printing, give sharp, clean-cut impressions when discharged on previously dyed grounds.

Various discharging agents of the usual well-known oxidising and reducing types have been suggested from time to time for use on viscose rayons, but while some of these may possibly have their own particular uses, it is generally recognised that reducing agents are the most efficient and the most widely applicable, and that of these the sulphoxylate-formaldehyde compounds are the best. In general practice, therefore, discharge styles on viscose rayons are confined to hydrosulphite discharges, though individual printers still, for some unaccountable reason, prefer other methods.

In regard to ground colours, the Direct dyestuffs and Azoic colours of the Naphthol A.S. range are of principal interest and are universally used for the style; other types, *e.g.* Vat colours and Indigosols, are occasionally used for special purposes, but neither accounts for more than a small proportion of the total output, though both are finding increased employment for the production of light and medium shades in response to the growing demand for fast colours.

The methods of obtaining discharge effects on viscose rayon and all-cotton goods respectively are substantially the same, though the dyeing of the former with Direct dyestuffs calls for careful manipulation and, frequently, some slight modification of process in order to avoid the unevenness arising out of the irregular dyeing affinities inherent in viscose yarns. To a great extent this difficulty has been overcome by the introduction of special Direct dyestuffs which will be noted later.

Discharging of Direct Colours.—Different lots, and sometimes the same lot, of viscose and other synthetic fibres of the regenerated cellulose group, exhibit considerable variation in their affinity for Direct cotton colours, and many of these dyestuffs, that give perfectly level shades on cotton, yield uneven results on viscose and other members of its group. The factors governing the production of a uniform quality of viscose are extremely difficult to control exactly on a manufacturing scale, and slight fluctuations in the conditions of

process appear to cause disproportionately large inequalities in the dyeing affinity of the finished product. These inequalities are particularly noticeable in the dyeing of skeins or hanks ; out of a number of hanks dyed together, some may be light, others dark, and yet others partly light and partly dark in shade.

In piece goods this irregularity in dyeing properties assumes the form of light or dark " bars " extending across the width of the piece from selvedge to selvedge. The appearance of such bars marks the introduction, during weaving, of a cop of viscose yarn of a dyeing affinity differing from that of the preceding and following yarns (cops). More rarely " barring " may be caused by varying tension in the weaving process, or by the inadvertent use of a different yarn ; but, as a rule, it is due to inequalities in the viscose fibre itself.

Although many ordinary Direct dyestuffs fail to cover up the irregularities in the dyeing affinities of commercial rayons, there are, nevertheless, others of the group which are suitable for the purpose and give more or less even shades. The range of such dyestuffs is, however, neither altogether satisfactory nor very complete ; it certainly comprises a large number of dyestuffs of different makers, but so many of these are closely allied to each other in chemical structure, properties, and shade that, from a dyeing point of view, they are practically identical, and thus the range is not really extended by their inclusion. Again, amongst the Direct cotton colours there was a notable paucity of dyestuffs suitable for the production of solid, even shades of blue. These gaps have now been largely filled, and a fairly comprehensive range rendered available, by the introduction of the Icyl (I.C.I.), Rigan (S.C.I.B.) and Benzo Viscose (I.G.) dyes which, although entirely new products prepared specially for covering up the dyeing inequalities of commercial viscose, belong as a class to the Direct colour group and, being applied by the same means, may be used in combination with suitable Direct colours for the dyeing of level compound shades on viscose fabrics. The Visco colours (Sandoz) also fall into the same category.

The best results as regards the levelling-out of inequalities are obtained by dyeing at a temperature of 185°–200° F. (85°–95° C.) in a bath containing as little Glauber's or common salt as possible, or better still, none at all. At lower temperatures the unevenness is more pronounced and the contrasts greater ; the presence of Glauber's salt also accentuates the tendency of the viscose to take up the dyestuff irregularly. The dyeing, operated in this manner, differs somewhat from the usual method of dyeing Direct colours and, as might be expected in the absence of saline assistants, the bath is not completely exhausted. Exhaustion, however, is not desirable ; the dyestuff must be retained, up to a point, in solution in the dye bath and not unduly forced (by additions of salts) on the more absorptive portions of the material.

It is obvious that goods withdrawn from the dye bath and still saturated with unexhausted dye liquor must not be allowed to lie wet for any length of time, as dyeing will still go on with the consequent production of uneven and patchy shades. The goods must be washed and dried with the least possible delay. Such dyeings as require after-treatment with formaldehyde, etc., or diazotising and developing, are dealt with in the usual manner after washing and before drying.

In the event of the material being known to be of equal dyeing quality throughout, the dyeing may, of course, be carried out in the normal manner, using Glauber's or common salt as described for dyeing cotton alone.

Another difficulty that crops up in the dyeing of all piece goods containing cotton and viscose is that although both fibres possess an affinity for Direct colours they do not possess it in an equal degree. In the dyeing of such colours

as dark browns and navies on mixtures of viscose and unmercerised cotton, the viscose takes up more colour than the cotton. This trouble is pronounced only in the case of dark shades, and there is no remedy for it, but its effect may be very much minimised by dyeing at relatively low temperatures (120°–140° F.) and using as little Glauber's salt as possible, or none at all.

In mixtures of viscose and mercerised cotton the opposite effect obtains, the cotton, particularly in pale shades, dyeing up darker than the viscose. Both fibres dye fairly evenly in dark shades, sufficiently so, at any rate, to be passable, but pale shades are almost impossible to equalise unless an excessive amount of salts is employed, and this, of course, tends to the formation of "bars" if the viscose is of variable dyeing quality. Viscose-mercerised cotton mixtures are rarely met with in printing cloths, and the difficulties in dealing with them are of little interest to printers in general.

In the production of discharge effects on viscose and other regenerated cellulose rayons, using Formosul or Rongalite as discharging agent, a selection of suitable dyestuffs for ground shades—that is even-dyeing dyestuffs which are destroyed completely by sulphoxylate-formaldehyde compounds—may be made from any of the numerous groups of Direct colours on the market; one group is as good as another. Space forbids the inclusion here of a full list of these colours, but the following selection of dyestuffs, manufactured by Imperial Chemical Industries, will serve to indicate the type of colour required for subsequent printing with white and coloured discharges. Corresponding colours of other groups, if preferred, may be found by reference to the *Colour Index* of the Society of Dyers and Colourists.

DIRECT DYESTUFFS.

* Chlorazol fast yellow 5 G.K.S.	*Chlorazol fast helio B.K.S.
* Chrysophenine G.S.	* ,, ,, ,, 2 R.K.S.
Chlorazol fast scarlet 4 B.A.S.	* ,, blue B.S.
,, ,, red K.S.	,, ,, 3 B.S.
* ,, ,, ,, F.G.S.	,, ,, R.W.S.
* ,, ,, rubine L.F.	,, fast blue F.F.K.S.
* ,, ,, bordeaux L.K.	,, sky blue G.W.S.
,, violet N.S.	,, dark green P.L.S.
,, ,, W.B.S.	,, green B.N.S.
,, ,, R.S.	,, orange brown B.X.S.
* ,, brown G.S.	,, drab R.H.S.
,, ,, B.S.	* ,, fast black B.K.S.
,, ,, M.S.	* ,, black S.D.S.
,, ,, L.F.S.	,, ,, E.S.
	,, ,, B.H.S.

Colours marked with an asterisk are specially suitable for level dyeing on irregular-dyeing viscose.

ICYL COLOURS.

Icyl orange G.S.	Icyl blue G.S.
,, ,, R.S.	,, ,, 2 R.S.
,, red G.S.	,, navy B.
,, brown G.S.	,, violet B.S.
	,, blue black 6 B.S.

The Rigan, Benzo Viscose, and Visco series are similar in dyeing properties to the Icyl colours, and all give even shades on irregular-dyeing viscose.

Ground shades of superior fastness to washing and soaping are obtained by the use of certain Direct dyestuffs containing free amino-groups which may be

diazotised and developed on the fibre or coupled with diazotised *p*-nitraniline. By these processes the shades are modified, or even entirely changed, and the all-round fastness is considerably increased. The fastness of many dyestuffs may also be improved by various other after-treatments, of which that with formaldehyde is most generally useful for discharge styles. Details of these processes are to be found in any modern treatise on dyeing [1] and are too well known to need elaboration here.

A few representative examples of these types of dyestuffs are cited below :—

(*a*) Diazotised and Developed Colours.

Chlorazol black B.H.S. (I.C.I.).	Triazogen orange R. (I.G.).
,, ,, S.D.S. (I.C.I.).	Diazamine blue B.R. (Sandoz).
,, ,, J.H.S. (I.C.I.).	Diazo fast blue 6 G.W. (S.C.I.B.).
,, diazo blue 2 B.S. (I.C.I.).	Diazo brilliant scarlet R.O.A. (I.G.).
,, brown M.S. (I.C.I.).	Diaminogene sky blue N. (I.G.).
Icyl blue black 6 B.S. (I.C.I.).	Diamine azo scarlet 8 B. ex. (I.G.).

(*b*) Coupled Colours.

Chlorazol brown M.S. (I.C.I.).	Various browns and blacks of the Para and Diamine Nitrazol groups, etc. coupled with *p*-nitraniline.
,, ,, G.M. ,,	

(*c*) Colours After-treated with Formaldehyde.

Visco black N. (Sandoz).	Formal black G. (Geigy).
Chlorazol brown M.S.	Chlorazol black E.S.

etc.

Vat colour discharges printed on grounds after-treated as under (*a*), (*b*), and (*c*) yield results which, though duller in effect as regards ground shades generally, are much faster than the ordinary discharges on untreated Direct colour dyeings.

Printing Colours.—The printing colours used for discharge work on dyed viscose rayons are precisely the same as those employed for the corresponding styles on all-cotton goods, and recipes for their preparation will be found under the heading of "Hydrosulphite Discharges on Direct Colours" (*q.v.*).

By far the greater proportion of discharge effects on viscose rayon are produced by means of Basic dyestuffs and hydrosulphites, with or without an addition of tannic acid to the printing colour. If tannic acid is omitted from the printing colour it is essential, in order to ensure fixation of the dyestuff on the fibre, that the dyed goods be prepared previously by padding through a solution of tannic acid itself or, alternatively, through a solution of one of the synthetic tannin substitutes such as Katanol O.N. As a precaution against "scumming" it is advisable to add a small percentage of either sodium chlorate, Resist Salt L., or Ludigol. The last two bodies are organic oxidising agents which act similarly to sodium chlorate by neutralising the reducing action of the small quantities of Rongalite or Formosul which, during printing, are almost always transferred to the face of the dyed cloth from the imperfectly cleaned unengraved parts of the copper rollers, and impair the solidity of the ground shade by partially discharging it during the subsequent steaming operation. In steaming, also, the chamber of the Mather-Platt

[1] *A Manual of Dyeing*, Knecht, Rawson, and Loewenthal (C. Griffin & Co., Ltd.); *Synthetic Dyestuffs*, Cain and Thorpe (C. Griffin & Co., Ltd.); *The Bleaching, Dyeing, and Chemical Technology of Textile Fibres*, S. R. and E. R. Trotman (C. Griffin & Co., Ltd.).

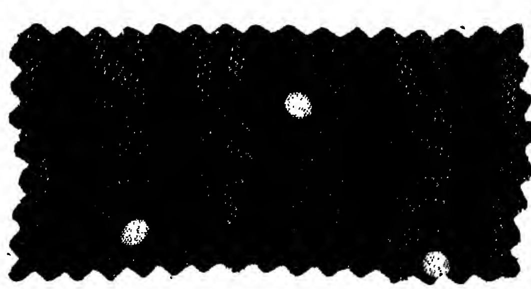
rapid ager becomes charged occasionally with fumes of sulphur dioxide and formaldehyde (decomposition products of sulphoxylate-formaldehyde compounds), both of which exert a reducing action on the ground shade and, thus, tend further to impair the quality and solidity of its colour. In these circumstances the use of Resist Salt L. or Ludigol again protects the ground colour from damage and yet introduces no element of danger from over-oxidation, which is liable to occur when sodium chlorate is employed as anti-scumming agent. Sodium chlorate in the presence of sulphur dioxide and steam is apt to act too energetically and destroy the ground which the object of its addition is to preserve.

During recent years the use of Vat dyestuffs as illuminating colours in the better classes of discharge work has increased to a notable extent on account of their superior fastness. In reality they are too good for the purpose, except on Azoic colour grounds, but unfortunately there are no others to replace them. Their application is according to the standard Rongalite-potash methods, adding extra Rongalite or Formosul as required ; but, being much faster than the grounds upon which they are printed, their normal after-treatment (chroming and soaping at the boil) must be moderated to conform to the inferior fastness properties of the grounds. This is particularly the case with dyeings of Icyl, Rigan, and Benzo Viscose colours, which are somewhat looser to washing, etc., than ordinary Direct dyestuffs.

Treatment after Printing.—The goods after printing are carefully dried and then steamed for 4–5 minutes in a hydrosulphite ager at 100°–102° C. (212°–216° F.) after which they are preferably allowed to lie for some time in order partially to re-develop (by air oxidation) the leuco compounds of the Basic or Vat dyestuffs used as illuminating colours. Thereafter the treatment follows the usual procedure adopted for cotton goods, viz. in the case of Basic discharge colours with tannic acid as mordant a passage through a fixing bath of tartar emetic, followed by chroming, washing, soaping lightly (if necessary), washing, and drying. These final operations are most conveniently and safely carried out in an open soaping range provided with the necessary compartments and adjusted to run easily without imposing undue stress and strain on the material. The treatment in tartar emetic is not necessary, and is omitted, where Katanol O.N. has been employed as mordant for Basic colours, or where Vat dyestuffs have been used for the discharge effects.

In the case of Vat colour discharges it is often necessary to soap the goods for the purpose of developing the full shade, but in view of the fact that the grounds are looser than the printed colours, it is advisable to soap more lightly (say at 120°–140° F.) than is customary for Vat colour prints.

The following pattern illustrates the popular black and white print produced by discharging a direct-dyed black.



Visco Black N. discharged with Hydrosulphite (Sandoz.).

BLACK GROUND.

Dyed with 10 per cent. Visco black N.
Washed and after-treated with—
$\begin{cases} \text{3 per cent. formaldehyde.} \\ \text{2 per cent. acetic acid 40 per cent.} \end{cases}$
Washed and dried.

WHITE DISCHARGE.

200	grms.	Hydrosulphite R.F.N. (or Formosul).
180	,,	water
20	,,	glycerine.
600	,,	Arabic gum 1 : 1.
1000		

After printing, the goods were steamed, washed, and then soaped at 60°–65° C. (140°–150° F.) for ten minutes. Soaping is essential to ensure pure whites and to develop fully the shade of any Vat dyestuffs that may also form part of the pattern discharged. The black, dyed as above, withstands this treatment perfectly, without a trace of bleeding, and is an excellent example of the fastness possessed by some of the after-treated Direct dyestuffs.

Discharging of Azoic Colour Grounds.—The combination of Vat colour discharges with Azoic colour grounds constitutes one of the fastest and most brilliant of all styles of textile printing ; and, as such combinations are as applicable to regenerated cellulose rayons as to cotton itself, they form an important branch of the rayon printing industry.

The Naphthols and Brenthols of the A.S. series now available, in conjunction with the Fast Colour bases, render possible the production of a complete colour scale, comprising a variety of yellows, oranges, reds, pinks, bordeaux, browns, navy and pale blues, violets, and one rather dull green. The range still lacks bright green shades, brilliant sky blues of the Chlorazol sky blue F.F.S. and G.W.S. types, and the quieter mode shades (grey, fawn, slate, beige, etc.) which are very difficult to dye evenly with Azoic colours and are better obtained by other means. But for full rich shades of the colours in the above-mentioned scale the Azoic colours are unsurpassed for brilliancy and fastness.

Most of the Naphthol A.S. and Brenthol A.S. colours are of excellent fastness to chlorine and hot soaping ; many of them are of good fastness to light, and a few are as fast generally as the best Vat colours. They are not all dischargeable, but, out of the enormous number of possible combinations, there remains a remarkably complete and fine range of easily dischargeable colours which fulfil most demands made upon them for variety.

As in the case of Direct colour grounds, the discharging of Azoic colour grounds on viscose rayon fabrics is operated by the same processes as those applied to the corresponding styles on cotton, and the same recipes and methods are equally applicable to both fibres. In preparing rayon goods with naphtholate [illegible] however, advisable to pad at a temperature of 60°–80° C. (1[illegible] for the reasons already given in the description of the direct pri[illegible] grounds. This and the more careful handling [illegible] between the treatment of the two materials.

Basic colour discharges present certain difficulties, especially when white and coloured effects are to be printed in multicoloured patterns, since Basic colours, steamed only in the rapid ager, preclude an energetic treatment in hot soap baths. This limits their use to the most readily dischargeable Azoic

colour grounds, for which a hot soaping is not absolutely essential either to clear the discharges or to develop the true shade of the ground colour. In any case Basic colours are employed only for work of inferior fastness, where the greatest possible brilliancy is of more importance than consistent fastness throughout the print.

On the other hand, Vat colour discharges are as fast as, and more often than not faster than, the ground shades and will withstand any amount of treatment that is necessary to bring up the full beauty of both ground and discharges.

PRINTING AND AFTER-TREATMENT.—The goods, having been dyed by any of the methods described for cotton, are printed with any of the various discharge colours described in the section entitled "Naphthol A.S." They are then steamed as usual for 4–5 minutes in the rapid ager and finished off according to their several requirements.

Basic colour discharges, together with any Chrome colours that may have been printed along with them, are fixed in tartar emetic, chromed, washed, very lightly soaped, washed again, and dried. Vat colour discharges are chromed, washed, soaped at the *boil*, washed, and dried.

A difficulty that arises in connection with discharges on Azoic colour grounds is due to the fact that certain Naphthol or Brenthol A.S. combinations are liable to "blind" or mask the lustre of viscose rayons on treatment with hot soap solutions (*Dyeing with Coal Tar Dyestuffs*, C. M. Whittaker, 1926, p. 219). This blinding effect has been investigated by Rowe (*Journ. Soc. Dyers and Colourists*, 1926, p. 208; *Artificial Silk*, Reinthaler-Rowe, p. 196), who states that "the lustrous non-blinded fibres consist of a true solution of the colouring matter in hydrated cellulose, whereas the blinded fibres consist of a suspension of microcrystalline aggregates of the colouring matter which are evenly disseminated throughout the colourless fibres. The coagulation or crystallisation of the colouring matter within the fibres is solely a temperature effect, and the blinded fibres are actually as lustrous as the non-blinded, but the particles of solid colouring matter in the former mask the lustre." Further, Rowe concludes that blinding is due solely to the formation of these crystalline aggregates of colouring matters produced by certain Naphthol A.S. combinations and *not* to the use of particular Naphthols as such, nor really to the boiling soap treatment, which has no blinding effect whatever on viscose rayon.

Combinations of Naphthol A.S.-R.L./Fast orange salt G. and Naphthol A.S.-B.O./Fast orange salt G. are particularly liable to blinding, whereas others such as—

Naphthol A.S.-D./Fast scarlet T.R. base,
,, A.S.-D./Fast red K.B. base,
,, A.S.-T.R./Fast scarlet T.R. base,
,, A.S.-T.R./Fast red T.R. base,

are free from the defect. Hence, when Vat colour discharges on Azoic colour grounds are in question, care must be taken to avoid using Naphthols and bases which are found to cause blinding when soaped at the boil. This restriction, however, does little to limit the scope of Azoic colours on viscose rayon, since there still remains a choice of non-blinding Naphthol A.S. combinations sufficiently wide to cover the whole range of the colour scale.

Discharging of Vat Colour Grounds.—The production of Vat colour discharge effects on dyed Vat colour grounds—a desirable style, but at all times difficult and harassing to work—is operated in the same manner as for cotton. The style was never produced in large quantities, and since the introduction

of the simpler and more reliable Indigosol resist processes, it has become almost obsolete.

White discharges on Vat colour grounds present no exceptional difficulties apart from the dyeing of even ground shades, and are still occasionally printed when special shades of extreme fastness, and too dark to be produced economically with Indigosols, are demanded.

Resist Styles on Viscose Rayons.

The relative weakness of regenerated cellulose fibres in the wet state precludes the application to viscose and similar rayons of many resist processes that are applied readily, and with safety, to the sturdier cotton fibre.

The processes most suitable for this class of work may be divided into two groups, viz.:

(*a*) Resists under padded grounds of—
- Aniline black.
- Azoic colours.
- Indigosol colours.

(*b*) Resists under printed covers of—
- Aniline black.
- Paramine brown, etc.
- Indigosol dyestuffs.
- Vat dyestuffs (Leucotrope resists).

With the exception of resists under Aniline black pads, all the foregoing processes may be successfully carried out by the methods employed for cotton, to which reference may be made for details.

It may be noted that resists under Azoic colours are practically confined to grounds of Variamine and Dianisidine blues and of Fast violet B. base or salt, using aluminium sulphate as resisting agent. Other grounds and resisting agents may, of course, be used if desired, but the effects so obtained are produced far better by discharging methods, which are now almost universally employed in current practice.

Aniline Black Resists.—Resist effects under Aniline black pads may be obtained by any of the many processes already described elsewhere in this volume; but if the lustre of the whole surface of the material is to be preserved, only such processes as are free from plastic bodies, *e.g.* zinc oxide, chalk, etc., must be employed.

Of the foregoing, the *Browning Process* (*q.v.*) is a good example and yields excellent results. It is rather a long process, however, involving as it does a preparation of the cloth with tannate of antimony and an open soaping previous to padding with Aniline black, and at the present time it is rarely used, having been superseded by more expeditious methods in which zinc acetate (eventually ferrocyanide) is employed as fixing agent for the Basic dyestuffs in place of tannate of antimony. Thus—

ZINC-SODIUM ACETATE RESISTS UNDER ANILINE BLACK.

(1) Print, on white rayon, resist colours made up on the following basis :—

PRINTING COLOUR.

20	grms.	Basic dyestuff.
30	,,	Fibrit D. (or acetic acid or methylated spirit).
150	,,	water.
800	,,	Resist Paste Z.A. (overleaf).
1000		

RESIST PASTE Z.A.

250 c.c.	zinc acetate 100° Tw.
250 ,,	water.
250 grms.	sodium acetate.
350 ,,	British gum.

Make up to 1000 c.c.

Suitable Basic dyestuffs for the style are: Astraphloxine F.F., Astra violet F.F.D., Thionine blue G.O.O., Methylene blue N.S.S., Rhodamines B. and 6 G.D. ex., Thio violet 5 R., Thioflavine T., Auramine O., Rhoduline sky blue 3 G., Xanthoacridine orange M.O. and Acridine orange R.S. It must be understood that these represent a selection only, many other Basic dyestuffs being equally suitable. For mode shades of grey, etc., which are difficult to obtain satisfactorily from Basic dyestuffs, it is preferable to use colours of the Modern grey R.C.N. and Modern violet types, which form fairly fast lakes with zinc mordants, and may be toned as required with Basic colours.

(2) After printing, the goods are dried well and nip-padded in the customary manner with a slightly thickened ferrocyanide-aniline black liquor, then being dried immediately over steam-heated cylinders.

(3) The goods are then steamed for 2–3 minutes at 104°–110° C. (220°–230° F.) in a high-temperature rapid ager, with the ventilator full open, and all side coils and chests heated. Lower temperatures may be used for steaming, but the discharge colours are not so well fixed nor does the black withstand greening influences so well as when development occurs at the higher temperature. Steaming completed, the goods are finished by chroming, washing, and drying on an open soaping range, soaping generally being omitted.

Much faster resist effects are produced on Aniline black grounds by the use of Vat, Rapid Fast, and Rapidogen dyestuffs, all of which are applied by the methods described for cotton. The difficulty with these dyestuffs is that they are very liable to run in padding and so give halos of white around the printed objects. For this reason they are less popular with printers than the Vat colour discharge style on dyed grounds of the faster Direct blacks such, for example, as Visco black N. or Formal black G. after-treated with formaldehyde. Many of the Vat colour reds and oranges discharged on Direct-dyed blacks are not only extremely fast, but also almost as bright as Azoic colours of the same shade; and other Vat colour discharges are, of course, as fast and bright as the same colours printed by resist methods.

From the foregoing *résumé* of the methods of printing regenerated cellulose rayons it will be obvious that, in the main, these materials may be dealt with as if they consisted merely of cotton. They demand more careful handling than cotton, however, and certain cotton styles that require heavy treatment in the way of dunging, dyeing, soaping, etc., are inadmissible; but, in general, the technique is the same for both classes of materials, and such slight modifications of process as are called for in dyeing and other processes are matters of detail rather than principle.

(II.) CELLULOSE ACETATE RAYONS.

Rayons of this particular group—Celanese, Rhodiaseta, Lustron, Seraceta, etc.—possess properties which differentiate them sharply from all other textile materials. The fibres consist of *cellulose esters*, not pure cellulose,

and, as might be expected from their difference in chemical composition, their affinity for dyestuffs differs widely from that of other synthetic fibres composed of pure cellulose, *e.g.* Viscose, etc., and also from that of the natural fibres, cotton, flax, silk, and wool. Their behaviour towards dyestuffs is markedly characteristic. Thus, Basic dyestuffs and Chrome colours of the Gallocyanine group fix upon cellulose acetate fibres without the aid of a mordant, and a few, but a very few, Acid wool dyes give satisfactory shades in dyeing; but, for the important group of Direct-dyeing cotton colours, cellulose acetate fibres exhibit no affinity whatever except in the isolated case of Chlorazol fast orange G.S.; nor are the Azoic colours applicable satisfactorily by any of the methods in general use, save in their special form of Rapid Fast and Rapidogen colours, which find a limited use in printing. Altogether, therefore, the cellulose acetate fibres may be said to possess little or no affinity for the great majority of dyestuffs normally employed for the colouring of other fibres; and of the small minority of such dyestuffs, many which are suitable for dyeing are of no use at all for printing. When Celanese, the prototype and most important of the acetate rayons, was first introduced, the difficulties encountered in printing and dyeing it satisfactorily (due to the lack of appropriate dyestuffs) seriously threatened to imperil its commercial development. To-day, thanks primarily to the pioneer research work of British chemists, that danger has been averted, and, at the present time, there exist several valuable and fairly complete ranges of new dyestuffs and dyestuff preparations which are specially adapted to the printing and dyeing of cellulose acetate fabrics or *acetate rayons*. Unfortunately, these dyestuffs have no affinity for other cellulosic fibres; but probably a series of "omnibus" colours will be developed later—homogeneous colours which will give even shades on various mixtures of cellulose acetate with other fibres.

Another trouble which arises in connection with the printing of acetate rayons is due to the fact that they are comparatively difficult to "wet out" or penetrate with the liquids usually employed for the preparation of printing colours. The effect of acetylating the cellulose molecule is to replace one or more of its hydroxyl groups by acetyl radicles of which, theoretically, five may be introduced on the basis of the percentage composition being expressed by the formula $C_6H_5(OH)_5$. The water absorptive capacity or permeability of cellulose acetates is determined by the degree to which acetylation has been carried; as the acetyl value rises, the permeability falls, until a point is reached, *e.g.* tetracetate $[C_6H_6O(COOCH_3)_4]$, at and beyond which the acetate becomes quite impervious to water and, consequently, useless for any ordinary textile purpose. The less highly acetylated products or lower acetates of cellulose are free from this defect in proportion to the number of unreplaced hydroxyl groups they contain, and the nearer they approach pure cellulose in composition the better are they penetrated with water. For this reason, rayons of the Celanese group are manufactured from mixtures of the lower acetates, the balance between acetyl and hydroxyl radicles being adjusted to give the maximum of lustre consistent with sufficient penetrability for practical purposes. These rayons are never, however, so permeable as cotton and viscose rayons, and cannot as yet be printed or dyed satisfactorily with any but their own special dyestuffs or Basic colours.

Acetate rayons when treated with caustic alkalies, or their equivalents, are converted into cellulose, and if this treatment is controlled in such a way as to act only on the outer parts of the fibres it forms the basis of a process which renders possible the printing and dyeing of such rayons by the same methods and materials as are employed for cotton. This process of saponification or hydrolysis will be described later under "Discharge Styles."

Cellulose acetate rayons possess a brilliant lustre, are stronger in the wet state than viscose and other regenerated cellulose rayons and, generally speaking, are more elastic than the latter. On the other hand, they lose their lustre if subjected to excessive heat, and, for this reason, they require more than usual care in drying, soaping, dyeing, etc.; on no account must they be baked on hot drying cylinders, nor is it advisable in wet processes to exceed a temperature of 85° C. (185° F.)—soaping should not be carried out at above 75° C. (167°–170° F.) as a rule, though the temperature may be raised to about 80° C. (176°–180° F.) without detriment for a short time in a bath of neutral soap.

Preparation of Cellulose Acetate Rayons for Printing.

Cellulose acetate rayons are almost invariably sized, before weaving, with mixtures of oil and wax. Linseed and other cheap drying oils, which are largely used for this purpose, are frequently a source of trouble during subsequent processes owing to their conversion into more or less insoluble oxidation products which are somewhat difficult to remove from the fibre by any means appropriate to the treatment of acetate rayon. If allowed to remain, or incompletely removed, these products turn yellow on steaming and impart an undesirable " buffy " tinge to the whole body of the fabric. Goods known to contain linseed oil should be scoured as soon as possible, because the longer they are stored the more highly oxidised and insoluble does the oil become.

Flour and starch sizes, used for the cotton warps of union fabrics consisting of acetate rayon and cotton, may be removed in the customary manner by a preliminary treatment with malt extract, or other enzymes, such as pancreas gland products, according to the character of the sizing in question. Any starch or fatty matter remaining after *malting* is finally removed in the scouring and bleaching operations.

Scouring and Bleaching of Cellulose Acetate Fabrics.—Good results in printing and dyeing acetate rayon can be secured only when the goods have been subjected to a thorough scouring with slightly alkaline soap for the purpose of freeing them as completely as possible from the oils and starches employed as sizes in the manufacturing processes.

The necessary alkalinity of the scouring liquors is best obtained with ammonia. Caustic soda should be excluded from all scouring and bleaching operations because even dilute solutions in the cold partially saponify cellulose acetate fibres and produce a corresponding amount of pure regenerated cellulose on their surfaces, thus destroying their characteristic properties to a degree commensurate with the degree of saponification. Soda-ash is much less pronounced in its action on cellulose acetates, and is often used for scouring purposes along with soap; but nevertheless, at the temperature of scouring, it also causes sufficient saponification to be troublesome in the printing and dyeing of union goods composed of acetate rayon and cotton (or viscose) and goods intended for the production of two-colour shot effects or acetate rayon resist effects. The presence of a thin coating of pure cellulose around the acetate rayon fibre does little to impair the lustre, but it does impart a certain affinity for Direct cotton colours, and, consequently, in the production of the above-mentioned shot and reserve effects it causes a modification of shade on the acetate rayon threads, or a staining of the white acetate rayon reserves, in the composite fabric. Soda-ash may be used safely for all purposes where a slight saponification is not injurious. Ammonia, on the other hand, has no action on acetate rayons at the strength employed in scouring, and it offers, therefore, the advantage that goods destined for any style of work, whether

100 per cent. Celanese or union fabrics, may be scoured together, whereby a great saving of time is effected in the charging and recharging of scouring becks.

Similarly, in bleaching with hydrogen peroxide and silicate of soda, the avoidance of free caustic alkali is essential if the characteristic features of acetate rayons are to be retained in full. To this end, the alkalinity of the bleaching liquor is neutralised, according to well-known precedent, with magnesium sulphate, a careful balance being maintained between the magnesium sulphate and the silicate of soda. Too much magnesium sulphate gives a poor white on the cotton part of union goods, whereas too little results in the saponification of the cellulose acetate portion. A practical proportion is—3 parts sodium silicate, 100° Tw., to 2 parts Epsom salts, both by weight.

Bleaching is rarely necessary in the case of materials composed entirely of cellulose acetate. Pure Celanese, and other 100 per cent. acetate rayons, are usually sufficiently well prepared for printing by a single good scour followed by a thorough wash, though occasionally they are improved by bleaching. On the contrary, unions and fancy weaves embodying Celanese and unbleached cotton always require bleaching, and often it is a difficult matter to obtain a good, permanent white on the cotton as, of course, the presence of Celanese makes it impossible to kier-boil the goods. Cotton which has not been kier-boiled under pressure with caustic soda is very liable to become yellow when steamed or stored for a considerable time, even though it appears to be a good white at the outset. If, by good chance, the goods happen to be woven with kier-boiled yarns, the production of a permanent white presents no difficulty.

A process of scouring and bleaching which is shorter than many steeping processes in general use, and yields an excellent white, is carried out as follows:

(1) *Scouring.*—The goods (acetate rayon-cotton unions, etc.), previously malted, if necessary, to remove farinaceous sizes, are treated in a bath of—

1500 litres water,
750 c.c. ammonia (0·880 sp. gr.),
3 kilos. soap,

for 2 hours at 80° C. (175° F.). As the ammonia volatilises during process, a further 750–1000 c.c. may be added in portions as required.

(2) The goods are washed well through two becks of water.

(3) *Bleaching.*—The washed goods are entered cold into a bleaching bath of—

1500 litres of water.
15 ,, silicate of soda 100° Tw.
30 ,, hydrogen peroxide 100 vols.
10–15 kilos. Epsom salts.

The goods are wetted out in the cold, and the temperature then raised to 80° C. (175° F.), the treatment being continued at this temperature for one hour.

(4) The goods are washed well, soured in sulphuric or hydrochloric acid to remove adherent magnesium hydrate, washed again thoroughly, hydro-extracted, and dried, preferably on a stenter.

The foregoing quantities are calculated for 75 kilos. of cloth. If desired, soda-ash at the rate of 1–1½ grms. per litre may be used in place of ammonia for scouring, but, as already noted, it has its limitations and may be injurious.

Other methods of bleaching with hydrogen and sodium peroxides, involving a steeping of the goods for several hours, or even overnight, in liquors at a

lower initial temperature (38°–50° C. or 100°–122° F.), are in current use and give quite satisfactory results.

Sodium hypochlorite (" soda chemic ") is also quite largely used as a bleaching agent, partly because it is cheap, and partly because some bleachers have a fear of tendering the fibre with peroxide bleaches. The white obtained with hypochlorites on cotton which has not been well cleansed by kier boiling has a greater tendency to turn yellow on steaming, or in storage, than that produced with hydrogen or sodium peroxide, and the material, as a whole, wets out less readily when bleached with hypochlorites than when peroxides are used for the purpose.

The hydrogen peroxide bleach just described yields excellent whites which are practically unaffected by prolonged steaming and, at the same time, it produces no undue tendering of either fibre in an acetate rayon-cotton fabric.

All operations connected with scouring and bleaching are best carried out on elliptical winch machines in order to avoid pull and strain on the material.

Printing of Cellulose Acetate Rayons.

Apart from the Basic colours and Indigosols (by a special process) none of the various groups of dyestuffs normally used for other fibres exhibits what may be termed a *group* affinity for cellulose acetate fibres, which are peculiarly inert in respect to ordinary textile colouring matters. Individual members of the Azoic, Azo acid, Alizarin, and Gallocyanine series, containing particular groupings of amino-, hydroxyl, and nitro-radicles, are, however, found to possess a certain affinity for acetate rayon, and from these dyestuffs, together with a few Basic dyestuffs, the earlier series of acetate rayon dyes were made up, as, for example, the Cellutyl group of Imperial Chemical Industries, Ltd. These were never satisfactory in regard to either range or fastness, nor were many of them particularly well suited to printing, and, so far as the printing of 100 per cent. acetate rayon is concerned, they have been displaced entirely by newer colouring matters, such as the S.R.A., Duranol, Dispersol, Celliton Fast, Cibacet and Setacyl dyestuffs, all of which display a strong direct affinity for cellulose acetate fibres and, virtually, for no others.

In the case of union fabrics composed of mixtures of acetate rayon with cotton, wool, silk or viscose rayon, compromises have, of necessity, to be made. If, for instance, it be required to produce solid even shades on the constituent fibres of a union material of this kind, it is only possible to do this in two ways, viz. (1) by applying such of the ordinary dyestuffs as can be fixed on both fibres by a common method, special or otherwise, or (2) by mixing appropriate ordinary dyestuffs with acetate rayon dyestuffs, the former fixing on the cotton, silk, etc., and the latter on the acetate rayon ; the shades of the two types of dyestuffs must, of course, be matched, *e.g.* Chlorazol fast pink B.K.S. (for cotton, silk, wool, or viscose) and Duranol red 2 B. (for acetate rayon), etc.

The application of the various classes of dyestuffs used in the printing of acetate rayon can be most conveniently dealt with under two separate heads, namely :

(A) The printing of Ordinary Dyestuffs.
(B) The printing of Acetate Rayon Specialities or Dyestuffs.

In this way, and by further grouping the dyestuffs according to their mode of application rather than according to their tinctorial qualities (reds, blues, etc.), a better appreciation of their possibilities will be obtained.

(A) Printing of Ordinary Dyestuffs on Acetate Rayon.

Included under this heading are Direct cotton colours, Basic colours, Chrome colours, Azoic colours, Vat colours, Indigosols, and colours produced on the fibre by oxidation.

(*a*) **Direct Cotton Colours.**—Although Direct dyestuffs have no affinity for cellulose acetate they may, nevertheless, be printed on acetate rayon provided that the rayon has been more or less saponified, either in the piece or locally. This latter effect can be produced by an addition of caustic soda to the printing colour ; on steaming, the acetate rayon is saponified on the printed parts only and as, in this condition, it acts exactly like pure cellulose, the Direct dyestuff is fixed upon it in the same way as it would be on cotton.

A printing colour made up on the following lines is equally adapted to the printing of 100 per cent. acetate rayon or to a mixed fabric of acetate rayon and cotton (or viscose rayon), but not to mixtures with silk or wool, which are destroyed by caustic soda :—

Direct Dyestuff Printing Colour.

25	grms.	Direct dyestuff.
50	,,	glycerine.
250	,,	water.

Dissolve and add—

500	grms.	British gum thickening 1 : 1.
90	,,	caustic soda 86° Tw.
85	,,	water.
1000		

Print, dry, steam for 1 hour in the continuous steamer, sour in weakly acidified water, wash thoroughly in warm water to remove the acid and thickening, rinse in cold water and dry.

For lighter shades, the above colour is reduced with an alkaline paste :—

90	grms.	caustic soda 86° Tw.
25	,,	glycerine.
285	,,	water.
600	,,	British gum thickening 1 : 1.
1000		

If Benzopurpurines are used for reds, the goods may require a run through a weak alkali before the final wash in order to restore the shade of the red, which has been blackened by souring.

Any Direct dyestuff which is suitable for the " crimp " style on cotton (*i.e.* which does not " mark-off " in the wet state in the presence of caustic alkali) may be printed safely by the foregoing recipe. Amongst some of the best for the purpose are :—

Benzopurpurine 4 B.P.S.
Brilliant geranine B.
Dianol brilliant blue 6 B.
Chlorazol sky blue F.F.S.
Sun yellow 3 G.
Chlorazol black E.S. (for greys).
Chlorazol fast red K.S.
Trisulphon violet B.
Thiazol yellow Z.
Mimosa Z.
Trisulphon brown G.
Chlorazol blue B.
Chlorazol brown P.B.S.

Oranges, greens, and olives are best obtained by mixtures of the above Sun yellow 3 G. with Dianol brilliant blue and Brilliant geranine B. in various proportions according to the shade required.

Excess of caustic soda in the printing colours must be carefully avoided, otherwise the acetate rayon is saponified too far and loses its lustre.

(*b*) **Basic Colours.**—As already stated, the Basic dyestuffs possess a direct affinity for cellulose acetate rayon, upon which they fix sufficiently well without the aid of tannic acid or Katanol mordant. Their application is exceedingly simple. Thus:—

Basic Dyestuff Printing Colour.

10	grms.	Basic dyestuff.
120	,,	acetic acid 50 per cent.
220	,,	water.
650	,,	Senegal thickening 1 : 1.
1000		

Print, dry, steam for ¾–1 hour in the open steamer, wash, and dry. An addition of tannic acid and, after steaming, a passage through a bath of tartar emetic, give slightly increased fastness to washing and light, but the use of these substances is not essential, unless the fabric printed contains cotton.

Unions of acetate rayon and silk or wool may be printed according to the foregoing method with or without the use of tannic acid; unions containing cotton, however, positively require an addition of tannic acid, followed by an after-treatment in tartar emetic (or, if printed without tannic acid, an after-treatment with Katanol O.N.), in order to fix the dyestuff on the cotton.

Of the vast family of Basic dyestuffs suitable for printing acetate rayon the undermentioned are to be recommended as typical of the range available:—

Auramines O.S., O., G.
Thioflavine T.
[illegible] T.S. and M.
Safranines.
Rhodamines 6 G.H. ex. and B.S.
Brilliant greens.
Acronol green B.S.
Astraphloxine F.F. ex.
Acridine oranges (all brands).
Turquoise blue G.S.
Victoria blue (all brands).
Methylene blue (all brands).
Malachite greens (all brands).
Astra violet F.F.D. ex.
Magenta (all brands).

The Basic dyestuffs are principally used for styles in which extreme brightness is the first consideration; for general work they are too loose to washing and light, and in actual practice they are very little employed at the present time.

(*c*) **Chrome Mordant Colours.**—Chrome colours of the Gallocyanine series (the only ones used for acetate rayon) combine the properties of Basic and Mordant dyestuffs. They are, in reality, Basic colours which, owing to the presence in their molecule of hydroxyl groups in the *ortho*-position to each other, possess also the property of forming lakes with metallic bases of which chromium oxide is, by far, the most important. As Basic colours, they have a definite affinity for cellulose acetate fibres, upon which they fix readily *without the use of any mordant*. If used for printing unions containing cotton, however, the necessary quantity of mordant, in the form of chromium acetate, must be added in order to ensure the fixation of the dyestuff on the cotton, or its equivalent, viscose rayon.

Several members of the Gallocyanine series require to be printed in a reduced state with an addition of sodium chlorate, which becomes active only during steaming and promotes the necessary re-oxidation of the dyestuff on the fibre to its insoluble form. Others, already in the soluble leuco-form, require no preliminary reduction; and yet others are better applied either without reducing agent (Rongalite, Formosul, etc.) or chlorate or both.

Examples of these different methods as applied to the more important Chrome colours used in printing on pure (100 per cent.) acetate rayon are illustrated in the table below.

CHROME COLOUR PRINTING PASTES.

	1.	2.	3.	4.	5.	6.
	grms.	grms.	grms.	grms.	grms.	grms.
Chromacetine Blue S. pdr.		..	..	..	..	..
Modern Violet pdr.	30	..	..	..	..	..
Blue 1900 pdr.		..	..	..	..	..
Violet P.D.H. pdr.	..	30	..	..	..	..
Prune pure pdr.	..	..	30	..	..	..
Solochromé Prune A.S. pdr.	..	..		50	..	..
Modern Grey P.S. pdr.	..	..	..	..	30	..
Phenocyanine V.S.N. paste	..	..	..	..	..	100
Indigosol developer G.A.	..	50	..	..	..	..
Hot water	267	212	334	100	220	..
Cold water	..	..	..	..	..	200
Rongalite C. or Formosul	3	8	6	..	..	..
Urea	..	..	..	..	50	..
Formic acid 90 per cent.	..	..	30	..	..	..
Acetic acid 40 per cent.	..	..	..	150	..	..
Heat up until the dyestuff is fully reduced and/or dissolved, then add—						
Gum Arabic or Senegal 1 : 1	600	600	600	700	680	600
Cool and add—						
Sodium chlorate 25 per cent. sol.	80	80	..	..	..	80
Turpentine	20	20	..	..	20	20
	1000 grms. each.					

Print, dry, steam for 20–60 minutes in a continuous steamer, wash and dry.

In the case of Prune pure (No. 3 above) the colour turns very green on steaming and takes a considerable time to re-oxidise and regain the correct dark reddish navy blue shade of the prune. The addition of chlorates is of no advantage in accelerating the re-oxidation, the best results being obtained by passing the printed goods, after steaming, through a bath of—

30 c.c. hydrogen peroxide (12 vols.).
3 ,, ammonia 25 per cent.
1000 ,, water.

at 45°–50° C. (113°–122° F.), followed by washing and drying. Hydrogen peroxide, at this strength, has no detrimental effect on other colours printed along with Prune pure.

Phenocyanine V.S.N. (No. 6 in table) is made up throughout in the cold. It gives an interesting pure blue shade not obtainable from other Chrome colours.

Oranges, greens, and olives are best obtained by mixtures of the above Sun yellow 3 G. with Dianol brilliant blue and Brilliant geranine B. in various proportions according to the shade required.

Excess of caustic soda in the printing colours must be carefully avoided, otherwise the acetate rayon is saponified too far and loses its lustre.

(*b*) **Basic Colours.**—As already stated, the Basic dyestuffs possess a direct affinity for cellulose acetate rayon, upon which they fix sufficiently well without the aid of tannic acid or Katanol mordant. Their application is exceedingly simple. Thus:—

BASIC DYESTUFF PRINTING COLOUR.

10	grms.	Basic dyestuff.
120	,,	acetic acid 50 per cent.
220	,,	water.
650	,,	Senegal thickening 1 : 1.
1000		

Print, dry, steam for ¾–1 hour in the open steamer, wash, and dry. An addition of tannic acid and, after steaming, a passage through a bath of tartar emetic, give slightly increased fastness to washing and light, but the use of these substances is not essential, unless the fabric printed contains cotton.

Unions of acetate rayon and silk or wool may be printed according to the foregoing method with or without the use of tannic acid; unions containing cotton, however, positively require an addition of tannic acid, followed by an after-treatment in tartar emetic (or, if printed without tannic acid, an after-treatment with Katanol O.N.), in order to fix the dyestuff on the cotton.

Of the vast family of Basic dyestuffs suitable for printing acetate rayon the undermentioned are to be recommended as typical of the range available:—

Auramines O.S., O., G.	Acridine oranges (all brands).
Thioflavine T.	Turquoise blue G.S.
Safranines T.S. and M.	Victoria blue (all brands).
Rhodamines 6 G.H. ex. and B.S.	Methylene blue (all brands).
Brilliant greens.	Malachite greens (all brands).
Acronol green B.S.	Astra violet F.F.D. ex.
Astraphloxine F.F. ex.	Magenta (all brands).

The Basic dyestuffs are principally used for styles in which extreme brightness is the first consideration; for general work they are too loose to washing and light, and in actual practice they are very little employed at the present time.

(*c*) **Chrome Mordant Colours.**—Chrome colours of the Gallocyanine series (the only ones used for acetate rayon) combine the properties of Basic and Mordant dyestuffs. They are, in reality, Basic colours which, owing to the presence in their molecule of hydroxyl groups in the *ortho*-position to each other, possess also the property of forming lakes with metallic bases of which chromium oxide is, by far, the most important. As Basic colours, they have a definite affinity for cellulose acetate fibres, upon which they fix readily *without the use of any mordant.* If used for printing unions containing cotton, however, the necessary quantity of mordant, in the form of chromium acetate, must be added in order to ensure the fixation of the dyestuff on the cotton, or its equivalent, viscose rayon.

Several members of the Gallocyanine series require to be printed in a reduced state with an addition of sodium chlorate, which becomes active only during steaming and promotes the necessary re-oxidation of the dyestuff on the fibre to its insoluble form. Others, already in the soluble leuco-form, require no preliminary reduction; and yet others are better applied either without reducing agent (Rongalite, Formosul, etc.) or chlorate or both.

Examples of these different methods as applied to the more important Chrome colours used in printing on pure (100 per cent.) acetate rayon are illustrated in the table below.

CHROME COLOUR PRINTING PASTES.

	1.	2.	3.	4.	5.	6.
	grms.	grms.	grms.	grms.	grms.	grms.
Chromacetine Blue S. pdr. / Modern Violet pdr. / Blue 1900 pdr.	30	..	..	..	..	..
Violet P.D.H. pdr.	..	30	..	..	..	..
Prune pure pdr.	..	..	30	..	..	..
Solochrome Prune A.S. pdr.	..	..		50	..	..
Modern Grey P.S. pdr.	..	..	..	..	30	..
Phenocyanine V.S.N. paste	..	..	..	..	..	100
Indigosol developer G.A.	..	50	..	..	..	..
Hot water	267	212	334	100	220	..
Cold water	..	..	..	..	..	200
Rongalite C. or Formosul	3	8	6	..	..	..
Urea	..	..	..	..	50	..
Formic acid 90 per cent.	..	..	30	..	..	..
Acetic acid 40 per cent.	..	..	..	150	..	..
Heat up until the dyestuff is fully reduced and/or dissolved, then add—						
Gum Arabic or Senegal 1 : 1	600	600	600	700	680	600
Cool and add—						
Sodium chlorate 25 per cent. sol.	80	80	..	..	..	80
Turpentine	20	20	..	..	20	20
	1000 grms. each.					

Print, dry, steam for 20–60 minutes in a continuous steamer, wash and dry.

In the case of Prune pure (No. 3 above) the colour turns very green on steaming and takes a considerable time to re-oxidise and regain the correct dark reddish navy blue shade of the prune. The addition of chlorates is of no advantage in accelerating the re-oxidation, the best results being obtained by passing the printed goods, after steaming, through a bath of—

30 c.c. hydrogen peroxide (12 vols.).
3 ,, ammonia 25 per cent.
1000 ,, water.

at 45°–50° C. (113°–122° F.), followed by washing and drying. Hydrogen peroxide, at this strength, has no detrimental effect on other colours printed along with Prune pure.

Phenocyanine V.S.N. (No. 6 in table) is made up throughout in the cold. It gives an interesting pure blue shade not obtainable from other Chrome colours.

The Chrome colours are used principally for the production of full navy shades, and are more generally applicable than the acetate rayon specialities, since by the addition of 70–100 c.c. of chromium acetate, 32° Tw., per litre of printing colour they may be printed to give fast level shades on unions of acetate rayon and cotton or viscose rayon.

(*d*) **Azoic Colours.**—The ordinary methods of producing Azoic colours on the fibre by impregnation with naphthols and development with diazo solutions are impracticable on acetate rayons unless the fibre is partly saponified; and for plain ground shades and for printing by these processes they are not employed. On the other hand, the Rapid Fast colours and the Rapidogens, both of which are applied in alkaline media, afford a convenient and efficient means of printing a full range of fast and bright Azoic colours on *unsaponified material*, whether of 100 per cent. acetate rayon, or of mixtures of this with cotton. Of course the printed parts are, to a certain extent, saponified, but not sufficiently so to interfere unduly with the lustre of the fabric provided that the alkali content of the colours is not excessive.

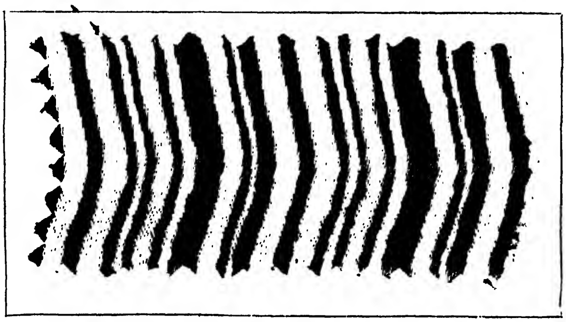
The methods customary for the printing of Rapid Fast and Rapidogen colours on cotton may be employed similarly on acetate rayon (see Naphthol A.S.).

It is to be noted that in the case of Rapid Fast colours brighter shades are obtained by hanging than by steaming the goods for the development of the colour.

(*e*) **Vat Colours.**—The Vat colours are employed in the printing of acetate rayon when the highest degree of fastness is demanded, and for this purpose they are unrivalled. They are applied by the normal methods as used for cotton, their fixation on acetate rayon being due entirely to the alkalinity of the printing colours, which brings about partial saponification of the cellulose acetate fibre, resulting in the formation of a certain amount of regenerated cellulose, upon which the colours fix as upon cotton itself.

Any Vat colour printing recipe may be used, but the various Rongalite-potash formulæ are generally preferred on account of their relatively mild action on the rayon fibre. If recipes containing free caustic soda are used, the caustic soda must be cut down to a minimum, otherwise the fibre may be completely saponified and lose its lustre altogether or become "blinded"—an effect sometimes aimed at, but not usually desirable. After printing, the goods are steamed and re-oxidised, etc., in the usual manner, care being taken to avoid all undue mechanical stress and strain and to conduct the soaping operation at a maximum temperature of 80° C. (175° F.).

The attached pattern has been produced by the following process:—



Indanthrene Printing Yellow G.O.K.
Indanthrene Printing Violet B.B.F. } on Acetate Rayon (I.G.).

	Yellow.	Violet.
Indanthrene printing yellow G.O.K. double paste	150 grms.	..
Indanthrene printing violet B.B.F. paste	..	150 grms.
Glycerine	40 ,,	..
Gum arabic 1 : 1	500 ,,	500 ,,
Potassium carbonate	120 ,,	..
Soda-ash	..	80 ,,
Rongalite C.	80 ,,	80 ,,
Water	110 ,,	190 ,,
	1000	1000

Print, dry well, steam for 5 minutes in the rapid ager at 100°–101° C. (212°–214° F.), pass through a bath containing—

2 grms. sodium perborate,
5 c.c. acetic acid 40 per cent.,
1000 c.c. water,

at 50° C. (120° F.), wash, soap lightly at 80° C., wash, and dry.

Recipes on the above lines may be utilised for printing any type of Vat dyestuff on acetate rayon or its mixtures with cotton, silk, or viscose rayon.

(*f*) **Indigosol Colours.**—These dyestuffs are particularly adapted to the printing of 100 per cent. acetate rayon and also to the production of interesting acetate rayon or cotton reserve effects and two-colour reserves on mixed fabrics of these two fibres.

None of the processes in use for cotton or viscose rayon is applicable to cellulose acetate rayon. Simple ageing or a short passage through an oxidising bath leaves the fibre practically unpenetrated, and such colour as does adhere is easily washed or rubbed off. The appropriate treatment for acetate rayons consists in steaming the goods, printed with a thickened solution of the dyestuff, for 10–20 minutes and afterwards developing in a hot bath of sulphuric acid and sodium nitrite for a longer time and at a higher temperature than are necessary for cotton. Under the influence of steam the dyestuff penetrates into the rayon fibre and becomes sufficiently fixed thereon, in the undeveloped state, to withstand a vigorous washing and even a light soaping without suffering any considerable loss in the depth of the ultimate shade obtained on subsequent oxidation. In similar circumstances, cotton goods printed with Indigosols would be more or less completely "stripped," *i.e.* the dyestuff would wash out. Conversely, *if the goods were not soaped or washed* after steaming, the dyestuff would remain unaltered on the cotton fibre and could be developed afterwards in the usual oxidising baths. On this difference between the behaviour of the two fibres towards Indigosols is based the production of several reserve effects to be described later.

The *direct printing* of Indigosols may be carried out in two ways, viz. (1) by adding the sodium nitrite, necessary for development, to the printing colour; (2) by introducing the nitrite into the developing bath.

I. Nitrite in Printing Colour.

50–80	grms.	Indigosol dyestuff.
30	,,	Glyecine A. or Dissolving Salt B., if required.
380–350	,,	water.
500	,,	tragacanth 65 : 1000.
30	,,	sodium nitrite.
10	,,	ammonia 25 per cent.
1000		

Print on 100 per cent. acetate rayon (Celanese, etc.), dry, steam for 15 minutes in a combined ageing and steaming machine or, alternatively, 2 or 3 times through a rapid ager, develop in a hot bath containing—

$$\begin{cases} 20 \text{ c.c. sulphuric acid } 168^\circ \text{ Tw.} \\ 1000 \text{ ,, water} \end{cases}$$

for 1½–3 minutes at 75°–80° C. (167°–175° F.), wash thoroughly, soap lightly at 60°–70° C. (140°–160° F.), wash, and dry.

A shorter and cooler development—for 20–30 seconds at 25°–50° C.—often gives perfectly satisfactory results.

II. Nitrite in Developing Bath.

	50–125	grms.	Indigosol dyestuff.
	415–340	,,	water.
	30	,,	Glyecine A., Fibrit D., or Dissolving Salt B., as required.
	500	,,	tragacanth 65 : 1000.
(optional)	5	,,	sodium nitrite.
	1000		

Print, dry, steam as before, develop for 8–10 seconds at 70° C. (160° F.) in a bath containing—

$$\begin{cases} 20 \text{ c.c. sulphuric acid } 168^\circ \text{ Tw.} \\ 1\tfrac{1}{2} \text{ grms. sodium nitrite.} \\ \text{per } 1000 \text{ c.c. water.} \end{cases}$$

(The sodium nitrite is added in the form of a very dilute solution so as to avoid evolution of nitrous gases.) Wash well, give a short soaping at 60°–70° C., wash, and dry.

Any Indigosol dyestuff, printed by either of these two processes (I. and II.), will give the same solid shade on acetate rayon, cotton or viscose fabrics provided that the operations of the after-treatment are carried out according to the particular sequence indicated; consequently both processes are well adapted to the production of solid prints of the ordinary type on union goods consisting of mixtures of any of the above-mentioned fibres.

If, however, Process II. is modified (1) by the interpolation of a washing and light soaping operation *after* steaming, or (2) by the omission of steaming altogether, it is possible, in mixed fabrics (1) to colour the acetate rayon fibres only, leaving the cotton fibres uncoloured, or (2) *vice versa*. For example, if the goods, printed by recipe II., are *steamed*, washed, and lightly soaped before development in acid and sodium nitrite, only the acetate rayon is coloured; whereas if they are developed immediately after printing, without being either steamed or washed, the cotton fibres only are coloured. Two-colour effects, the cotton or viscose one colour, the acetate rayon another, are easily obtained by compounding the processes, thus:—

1st Print Indigosol red H.R. (recipe II.), steam for 15 minutes, wash, soap lightly, wash, and dry.

2nd Reprint or cover with Indigosol O. 4 B. (recipe II.), dry and develop without further treatment in the acid-nitrite bath described, wash, and dry.

The result will be that the acetate rayon is coloured red, whilst the cotton is coloured blue.

In this manner a great variety of shot and other particoloured effects may

be produced on cotton cloths woven with ornamental patterns in acetate rayon. Similar two-colour effects, covering the whole surface of the material, may be obtained by padding, instead of printing, the Indigosols.

The *Soledon* colours may be applied in direct printing by the methods employed for Indigosols, but owing to their substantive properties they are not suitable for the two-colour styles last described.

Indigosol and Soledon colours, being in reality Vat dyestuffs, are very fast and bright, but their price and special, though simple, modes of application, together with the introduction of new acetate rayon dyes, have curtailed their use for general purposes.

(*g*) **Acid Colours.**—Although a few acid dyestuffs possess an affinity for acetate rayon, they are rarely employed in printing and are of no particular interest when they are printed. They may be made up as follows:—

10–30	grms.	Naphthalene orange G.S.
50	,,	glycerine.
340–320	,,	water.
600	,,	Senegal gum 1 : 1.
1000		

No acid or acid-yielding salt is required as in the cases of silk and wool printing.

After printing and drying, the goods are steamed, washed, and dried.

Amongst the colours suitable for printing may be mentioned:—

Metanil yellow Y.S., Citronine Y.S.,
Naphthalene orange G.S., Coomassie red G.S.,

and similar types of colours.

Though not used to any extent for printing, this type of dyestuff is occasionally employed for dyeing ground shades for discharge styles.

(*h*) **Oxidation Colours.**—The distinct affinity of cellulose acetate for aromatic amines and phenolic bodies is mainly of interest in printing for the production of fast black and brown colours from *p*-aminodiphenylamine, *p*-phenylenediamine, *o*-anisidine, and *p*-aminophenol, known in commerce respectively as Diphenyl black base, Paramine, Ortamine, and Fuscamine or Phenamine. Aniline black may be printed successfully only on saponified acetate rayon ; on 100 per cent. material it gives poor results.

The methods of application are analogous to those in use for cotton, and almost any formulæ in general use may be adapted to printing acetate rayon merely by substituting gum thickenings for starch pastes.

Diphenyl Black on Acetate Rayon (I.G.).

DIPHENYL BLACKS (Acetate Rayon).

		I.	II.	III.
		grms.	grms.	grms.
A	Diphenyl Black base	35	40	40
	Acetic acid 50 per cent.	65	100	150
	Lactic acid 50 per cent.	45	40	..
	Water	95	35	100
	Dissolve and add to—			
	Gum Senegal or Arabic 1 : 1	300	285	..
	Tragacanth 65 : 1000	..	..	300
	Cool.			
B	Thickening as above	300	285	250
	Water	95	152·5	105
	Sodium chlorate	30	22·5	30
	Aluminium chloride 52° Tw.	20	20	15
	Copper sulphide 30 per cent.	..	20	10
	Cerium chloride 85° Tw.	15	..	..
		1000 grms. each.		

Mix (A) and (B) in the cold immediately before use.

Print, dry, steam for 5 minutes in a Mather-Platt ager at 214° F. (101° C.), wash and soap lightly. The pattern illustrated was executed according to Recipe II.

If printed along with colours which require a longer steaming for their fixation, Diphenyl black is, preferably, first aged as above for 5 minutes to develop the black, and then steamed in the usual manner for 20–60 minutes in the continuous steamer. If passed into the latter directly after printing, along with an assortment of other and dissimilar goods, it frequently fails to develop at all.

The oxidation browns—Paramine, Fuscamine, and Ortamine—may be applied in several ways, of which those given below are the most generally useful.

PARAMINE AND FUSCAMINE BROWNS.

(a)	25	grms.	Paramine or Fuscamine G.
	2	,,	Rongalite C. or Formosul.
	175	,,	boiling water.
(b)	100	,,	British gum.
	100	,,	water.
	400	,,	tragacanth mucilage 60 : 1000.
(c)	25	,,	sodium chlorate.
	63	,,	water.
(d)	30	,,	ammonium nitrate.
	60	,,	water.
	20	,,	ammonium vanadate 1/1000.
	1000		

Mix (a) and (b), cool and add (c); just before use, add (d).

Ortamine Brown.

30	grms.	Ortamine D.
7·5	,,	hydrochloric acid 32° Tw.
25	,,	formic acid 90 per cent.
300	,,	boiling water.

Dissolve and add to—

500 grms. British gum-tragacanth thickening.

Cool and add cold—

15	grms.	sodium chlorate.
40	,,	water.
20	,,	potassium ferrocyanide.
62·5	,,	water.
1000		

Print, dry, steam for 5 minutes in a rapid ager at 101° C., wash, soap lightly, wash, and dry.

In multicolour printing, where a longer steaming is necessary, oxidation browns are treated like Diphenyl black (*q.v.*).

B. Printing of Acetate Rayon Dyestuffs.

From a practical point of view no heterogeneous selection from various groups of dyestuffs normally used for other fibres was ever fully satisfactory for printing acetate rayon, because it was impossible, from such diverse elements, to select a complete range of colours which were at once fast, bright, and of moderate cost.

The Vat dyestuffs and Indigosol and Soledon colours are, certainly, well adapted to the printing of acetate rayon ; they are bright and beautiful colours of excellent fastness, but they are usually considered too expensive for general purposes, and in the case of the Vat dyestuffs, in heavy patterns, there is some danger of reducing the lustre of the rayon ; moreover, their application is not of the simplest nature and requires careful attention if the best results are to be secured.

The increased demand for coloured acetate rayon fabrics and the practical difficulties encountered in printing and dyeing them with inadequate ranges of colours, indicated the necessity for the introduction of special dyestuffs possessing a definite affinity for cellulose acetate. The problem was tackled by the research staffs of British dyestuff manufacturers, and it is due to their valuable pioneer work that, to-day, there exist several complete ranges of fast dyestuffs particularly adapted to the direct printing and dyeing of acetate rayon. Unfortunately, many of these new dyestuffs cannot be discharged to a permanent white, so that, for the most part, their application is limited to direct printing and plain dyeing. It is to be anticipated, however, that this limitation will be removed as research proceeds to further successes.

The first of the true acetate rayon dyes were discovered by Green and Saunders (E.P. 197809, etc.) and were placed on the market by the British Dyestuffs Corporation, Ltd., under the name of *Ionamines*. These dyestuffs are prepared by converting various insoluble aminoazo- and aminoanthraquinone compounds into soluble methyl-ω-sulphonates which, whilst dissolving readily in cold or tepid water, are slowly hydrolysed on steaming (if printed) or in the hot dye bath, with liberation of the corresponding insoluble azo-base which is absorbed by, and fixes upon, the acetate rayon fibre in a regular and even manner. These aminoazo compounds act as Direct dyestuffs towards

cellulose acetate, yielding various shades of yellow and orange, but those which contain a reactive amino group may be diazotised and developed on the fibre with β-naphthol, β-hydroxynaphthoic acid or resorcinol and converted thus into various shades of scarlet, crimson, orange, purple, brown, navy, and bright blues and black.

The necessity for diazotising and developing most of the Ionamines in order to obtain any variety of interesting shades is a drawback to their application in printing, and for this reason they are little used save occasionally as dyed ground colours for subsequent discharging. There are, however, a few which may, if desired, be applied to direct printing, as for example :—

Ionamine red G.A.S.,	Ionamine blue B.S.
,, ,, K.A.S.,	,, orange C.B.S.

The colouring matter, dissolved in water and thickened with gum tragacanth or Senegal, is printed, dried, steamed, and washed in the customary manner. A small addition of oxalic acid to the printing paste assists in the fixation by facilitating the hydrolysis of the dyestuff.

The Ionamines may, perhaps, still be used to a small extent for dyeing, but for general purposes they are obsolete and, so far as printing styles are concerned, they have been completely superseded by newer products which yield similar results by simpler means and are as well adapted to printing as to dyeing—a great advantage. The principle underlying the application of these newer dyestuffs is that when certain types of insoluble colouring matters or organic compounds are presented in the form of colloidal solutions or suspensions to the cellulose acetate fibre, the fibre itself plays the part of a solid solvent of higher power than the original liquid solvent (or suspension or dispersion medium) and abstracts the colouring matter from the original solution, thus becoming dyed. This characteristic action of cellulose acetate furnishes some evidence in support of the solid solution theory of dyeing.

Although the above-mentioned principle, as related to the behaviour of insoluble dyestuffs and other organic bodies in a state of colloidal dispersion or pseudo-solution towards solid colloidal fibres, was not previously unknown (Pokorny, *Bull. Soc. Ind. Mulhouse*, 1893, 282 ; W. R. Dreaper, *Chemistry and Physics of Dyeing*, 1906), it received its first application to the dyeing and printing of Celanese at the hands of an English chemist, and was first embodied in practical form in the S.R.A. colours. Practically all dyestuffs now offered for acetate rayon are based on this principle and, with some variation in the solvents recommended by individual makers, they are all applied by the same methods.

The more important groups of these dyestuffs are summarised below :—

S.R.A.	(British Celanese, Ltd.).
Dispersol	(Imperial Chemical Industries, Ltd.).
Duranol	(,, ,, ,, ,,).
Cibacet	(Society of Chemical Industry, Bâle).
Celliton	(I. G. Farbenfabriken A.G.).
Celliton Fast	(,, ,, ,,).
Cellitazol	(,, ,, ,,).
Setacyl	(J. R. Geigy, Soc. Anym., Bâle.).

The relationship between these several groups of dyestuffs is that of different members of the same family. They are each built up of members of analogous classes of colouring matters, and each is in the form of a highly dispersed colloidal solution of insoluble particles, or capable of forming such a

" solution " with suitable " solvent " media. The S.R.A. and Duranol colours are the central types of the main group, and were the first of their kind to be put on the market. The S.R.A. colours comprise a variety of different classes of dyestuffs, dispersed in solutions of the higher fatty acids, and they vary considerably in fastness properties. The Duranol colours, on the contrary, consist at present of members of only *one* group of dyestuffs, the finely comminuted particles of which are held in aqueous suspension ; and, apart from the Vat dyestuffs, they are the fastest colours available for acetate rayon.

The terms *colloidal solution, pseudo-solution, suspension,* and *dispersion,* as applied to acetate rayon dyestuffs are, for all practical purposes, synonymous.

S.R.A. Dyestuffs.—The method of dyeing and printing cellulose acetate goods with colloidal solutions of insoluble dyestuffs and other organic compounds was discovered by G. Holland Ellis of the British Celanese Company (E.P. 219349, etc.), and it was at once recognised as an outstanding advance on existing methods of colouring acetate rayon. Ellis observed that insoluble unsulphonated aminoazo- or hydroxyazo-dyestuffs when ground with sulphoricinoleic acid or its alkali salts, the " oleines " of commerce, or soap, became so finely dispersed on dilution with water that they were capable of dyeing acetate rayon from a weakly alkaline bath at 70°–80° C. In addition to colouring matters of the azo-group, the patent literature mentions the application of the method to other organic compounds such as, for example, the colour bases of triphenylmethane, azine, oxazine, and thiazine dyestuffs, indophenols, Vat dyestuffs of the Indigoid group, and certain basic derivatives of the anthraquinones.

The S.R.A. dyestuffs, as marketed in paste form, consist essentially of dyestuff and sulphonated oils intimately ground together and ready for use in dyeing or printing by simple dilution with soap solution or gum thickening as the case may be. Whether each of the various groups of colouring matters covered by the patents of the British Celanese Company is actually represented in the commercial range of S.R.A. colours is a moot point, since no definite information on the subject is vouchsafed by the manufacturers.

The S.R.A. colours, having a direct affinity for the Celanese fibre, and requiring no special process or plant for their development and fixation, are as easy to manipulate as any other class of dyestuff. They are intermiscible in any proportions for the production of compound shades on acetate rayons and, although they possess no affinity for cotton, viscose, wool, or silk, they are applicable, in conjunction with other appropriate dyestuffs, to the dyeing and printing of various union goods.

In this connection the Direct cotton colours and neutral-dyeing Acid colours are compatible with S.R.A. dyestuffs and may, therefore, be used along with them in the same dye baths or printing pastes for the production either of solid shades or shot effects on fabrics consisting of mixtures of Celanese with cotton, viscose rayon, wool, or silk.

Dyeing of S.R.A. Colours.—The dyestuff paste is thoroughly stirred in case of possible settlement during storage. The quantity required for dyeing is then weighed out and to it is added about an equal weight of Turkey-red oil, Monopol Soap, or "Celascour." The mixture is heated under a steam pipe and boiling soap solution (10–20 grms. per litre) is added gradually while stirring vigorously. When a good solution or dispersion is obtained, the liquor is filtered through a cloth into the dye bath or machine, and sufficient water or soap solution (boiling) added to make up the necessary volume. Dyeing is conducted at different temperatures according to the class of goods in hand. For lustrous or "bright" materials the operation

may be carried out at temperatures up to, but not exceeding, 80° C. (175° F.); at higher temperatures the lustre is impaired. Dull or "matt" materials may be dyed at the boil. Dyeing goes on in an easy and regular manner similar to the dyeing of cotton with Direct colours. It may be carried out in any machine used for cotton cloth—jigs, dye becks, and the like—but for delicate fabrics it is preferable to dye in one of the newer wince dyeing machines, in which all pull and strain on the cloth are avoided. Dyeing is very frequently and conveniently carried out in the scouring bath.

The after-treatment of dyed goods consists simply in washing thoroughly in order to remove completely surplus dye liquor, soluble oils, and soap, followed by drying over steam-heated cylinders at not too high a temperature.

It should be noted that no more dye liquor should be prepared than is required for the work in hand. Once a dye liquor has been allowed to cool it is no longer suitable for re-use. If an extra quantity is required for shading or other purposes, it must be kept hot and stirred up; otherwise it is better to use fresh paste for each addition to the dye bath.

If desired, Celanese mixtures with cotton, viscose rayon, wool, or silk, dyed with S.R.A. dyestuffs, may be cross-dyed (in a separate bath) with any of the many "Celanese resist" Direct cotton colours and Acid colours supplied by various makers. Cross-dyeing is mostly employed for Celanese mixtures containing silk or wool in cases where the shade required cannot be obtained except by means of Acid colours which can only be dyed under slightly acid conditions.

Printing of S.R.A. Colours.—In general, S.R.A. dyestuffs are printed directly on to scoured and bleached Celanese from gum thickenings containing dyestuff and a swelling agent such as methylated spirit or diethylene glycol.

Example.

$\left\{\begin{array}{l}\text{600 grms. gum Senegal 1 : 1.}\\ \text{200 ,, water.}\end{array}\right.$

Stir into—

150 ,, S.R.A. dyestuff in paste form.

Mix and add—

50 grms. methylated spirit.

——

1000

Print, steam for 20–30 minutes in dry steam, wash, and dry.

The choice of suitable thickenings, and the conditions under which steaming is conducted, are important factors in the successful printing of Celanese goods. Both these points are more fully discussed in the following section under the heading of "Duranol and Dispersol Dyestuffs" (*q.v.*).

The groups of S.R.A. dyestuffs listed below have been selected as those most suitable for the purposes indicated.

I. S.R.A. Dyestuffs, Fast to Light, suitable for Furnishing Fabrics.

S.R.A. Fast golden yellow X.	S.R.A. Fast red VII.
,, ,, ,, ,, XII.	,, ,, ,, F.S.I.
,, ,, ,, ,, XIII.	,, ,, heliotrope I.
,, ,, ,, ,, F.S.I.	,, ,, blue XII.
,, ,, ,, orange I.	,, ,, ,, XIII.
,, ,, ,, ,, III.	,, ,, violet blue F.S.I.

II. S.R.A. Dyestuffs, Fast to Steam, suitable for Direct Printing.

S.R.A. Fast golden yellow F.S.I.	S.R.A. Fast heliotrope I.
,, ,, ,, ,, XIII.	,, ,, violet II.
,, Golden yellow IX.	,, ,, violet blue F.S.I.
,, ,, ,, R.T.A.	,, ,, blue IV.
,, Pure yellow R.T.A.	,, ,, ,, XII.
,, Fast golden orange I.	,, ,, ,, XIII.
,, Scarlet II.	,, ,, green blue I.
,, Fast red F.S.I.	

III. S.R.A. Dyestuffs recommended as Illuminating Colours for Discharge Styles.

S.R.A. Golden yellow R.T.S.	(Tin or Decroline method).
,, Pure yellow R.T.A.	(,, ,, ,,).
,, Scarlet II.	(Tin discharge method).
,, Fast heliotrope I.	(,, ,, ,,).
,, ,, violet II.	(,, ,, ,,).
,, ,, red F.S.I.	(,, ,, ,,).
,, ,, blue IV.	(,, ,, ,,).
,, ,, ,, XII.	(,, ,, ,,).
,, ,, green blue I.	(,, ,, ,,).

IV. S.R.A. Dyestuffs suitable for Dyeing Dischargeable Grounds.

S.R.A. Pure yellow III.
,, Fast golden yellow XIII.
,, Discharge golden yellow A.
,, Fast golden orange I.
,, Orange III.
,, Red I.
,, ,, III.
,, ,, V.
,, Discharge violet B.
,, ,, blue A.
,, ,, ,, B.
,, ,, base III. } Diazotised and developed with β-oxynaphthoic
,, ,, ,, IV. } acid for deep blues and black.

All are dischargeable with zinc formaldehyde-sulphoxylates, such as Decroline, Zinc formosul, etc.

With regard to the working of processes connected with the application of S.R.A. dyestuffs, it may be taken that the dyeing and direct printing of pure Celanese goods proceed in a fairly straightforward manner and present no more difficulty than does ordinary calico printing. The reverse is the case with discharge styles, which are by no means easy to produce in perfection. The trouble arises from the fact that the decomposition products of S.R.A. colours (in common with those of other similar dispersed dyestuffs) are retained tenaciously by the fibre and offer considerable resistance to all practicable attempts to remove them by washing or even hot soaping. These residual products impart a yellowish or brownish tint to white discharges—a tint which, if not always noticeable at the outset, gradually develops by oxidation and, in the case of white discharges on dark grounds, may eventually become a decidedly full-bodied buff. Some initial improvement may be effected by loading the discharge printing paste with zinc oxide, or other white pigment, which masks the objectionable yellow tint, but the effect of this

palliative is only temporary as the pigment washes off readily. Moreover, the pigment cannot be applied to large patterns except at the expense of destroying the lustre on the printed parts of the Celanese fabric—this of course also takes place with small, finely engraved patterns, but is practically unnoticeable and may be disregarded.

A fuller description of discharge styles with S.R.A. and other dispersed dyestuffs will be found in the following pages under title of "Discharge Styles on Acetate Rayon."

The S.R.A. colours supplied the first satisfactory solution to the difficult problem of printing and dyeing acetate rayon, and on account of this, and because also they comprise a complete range of brilliant shades of good fastness and of easy application, they occupy an important position, both historically and technically, in the textile colouring industry.

Duranol and Dispersol Dyestuffs.—Almost contemporaneously with the introduction of the S.R.A. dyestuffs it was discovered by J. Baddiley and A. Shepherdson of the British Dyestuffs Corporation, Ltd., and by W. Kilby of Morton Sundour Fabrics, Ltd., that cellulose acetate had a strong affinity for certain aminoanthraquinone compounds when these were presented to it in the form of colloidal suspensions in water or other more or less aqueous media (E.P. 211720, 224077, 246984). Typical examples of the aminoanthraquinones employed for this purpose are: 1 : 4-diaminoanthraquinone, α-methylaminoanthraquinone and methylated diaminoanthrarufin, which dye cellulose acetate in shades of violet, red, and blue respectively. Dyestuffs of this description, marketed under the name of Duranol dyes, yield bright shades which are much faster to light than those obtained from Azo dyestuffs; indeed, as a group, they are superior in all-round fastness to other acetate rayon dyestuffs.

The Duranol colours consist entirely of aminoanthraquinone derivatives, and are *not* dischargeable when dyed as ground shades.

The Dispersol colours, on the other hand, consist, with one exception, of aminoazo- or hydroxyazo-dyestuffs and all are dischargeable except one—Dispersol fast yellow A.S.

In other respects the two groups are virtually alike, and members of both may be mixed together without fear of interaction.

Duranol and Dispersol dyestuffs are supplied in paste and powder qualities, and in the Duranol series a " paste fine " quality is specially prepared for printing. The Dispersol pastes are sufficiently finely dispersed without further preparation. If desired, the powder brands may also be used for printing, but they are more difficult to incorporate smoothly with the printing paste and are liable to give uneven, if not " specky," shades.

From the following list it will be seen that, between them, the Duranol and Dispersol dyestuffs provide a complete range of colours of good fastness to light and washing.

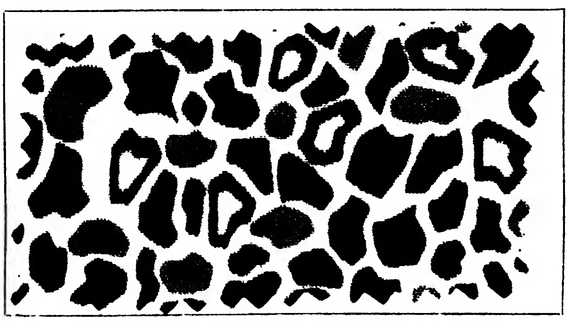
Duranol red 2 B.S.	Duranol brilliant blue C.B.S.
,, ,, X. 3 B.S.	,, ,, ,, G.S.
,, ,, G.S.	,, black C.B.
,, scarlet B.	,, ,, N.V.
,, ,, 3 B.	Dispersol fast yellow A.S.
,, ,, 2 G.	,, yellow 3 G.S.
,, light yellow S.	,, ,, C.Y.S.
,, brilliant violet B.S.	,, fast orange A.S.
,, violet R.S.	,, ,, ,, B.S.
,, ,, 2 R.S.	,, ,, scarlet B.S.

Duranol green B.S.	Dispersol fast brown 4 R.S.
,, maroon R.	,, ,, crimson B.S.
,, blue R.	,, ,, red A.S.
,, ,, C.B.S.	,, ,, ,, R.S.
,, ,, G.S.	,, black A.S.

In preparing printing colours from the foregoing dyestuffs it must be borne in mind that cellulose acetate is relatively difficult to penetrate or "wet out" with water. Hence, in order to obtain sharp impressions of the pattern, it is necessary to use thickenings of low water content, such as gum Senegal 1 : 1, gum Arabic 1 : 1, or British gum 1 : 1, which contain only 50 per cent. of water. If thickenings of high water content, *e.g.* gum tragacanth 65 : 1000, or locust bean gum 25 : 1000 (93·5 and 97·5 per cent. of water respectively), are employed, the prints are exceedingly liable to exhibit a mottled or "mealy" appearance, with ragged edges. The excess of water over that capable of being absorbed by the printed acetate rayon is squeezed out beyond the contours of the pattern and, carrying colour with it, it produces much the same effect as that obtained by pulling apart two sheets of glass between which a blot of paint has been pressed. This does not occur when stencilling through silk screens—so-called screen printing—and for this process gum tragacanth or locust bean gum may generally be used satisfactorily; also, occasionally, for the printing of such goods as crêpes and knitted fabrics, and in cases where a hard brittle thickening would tend to crack the fibres of delicate fabrics.

Printing colours of both Duranol and Dispersol dyestuffs may be made up simply by adding the dyestuff to the gum thickening, and often give satisfactory prints in this way. In most cases, however, it is found that an addition of glycerine improves the yield under average conditions of working and, generally speaking, glycerine, or similar hygroscopic bodies, forms a part of the printing colour, although its use is optional and may be dispensed with where conditions of steaming are favourable.

The general recipe given below represents the usual method of preparing printing colours, and has been used for the attached patterns; but it may be modified according to circumstances.



(I.C.I.)

Duranol Red X. 3 B.S., 200 grms. per Kilo.
,, ,, ,, 22·2 ,, ,,

General Recipe for Duranol and Dispersol Colours.

200 grms. Duranol or Dispersol dyestuff in paste.
50 ,, glycerine.
250 ,, water.
500 ,, gum Senegal 1 : 1.

1000

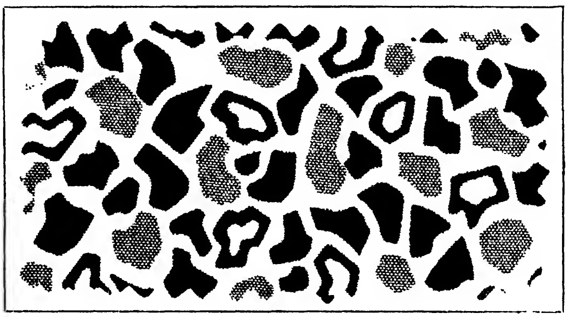
Reducing Paste for Light Shades:—

50	grms.	glycerine.
350	,,	water.
600	,,	gum Senegal 1 : 1.
1000		

Example.—Duranol red X. 3 B.S., 1 : 8 (=22·2 grms. per kilo.).

{1 part Duranol red X. 3 B.S., 200 grms. per kilo.
{8 parts reducing paste.

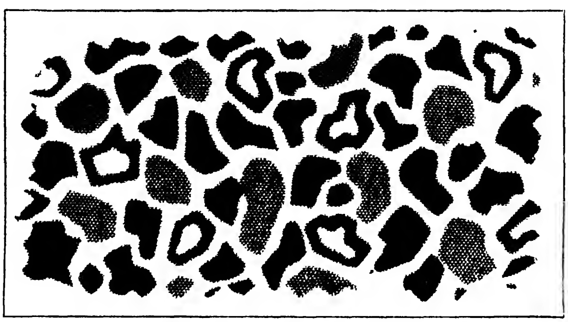
After printing the goods are carefully dried, steamed for 20–30 minutes without pressure in dry steam, washed, and dried.



(I.C.I.)

Dispersol Fast Red R.S., 200 grms. per Kilo. and 1 : 8.

A pure blue shade which does not sublime in steaming is obtained with Duranol brilliant blue G.S.



(I.C.I.)

Duranol Brilliant Blue G.S., 200 grms. per Kilo. and 1 : 8.

Print, steam, and wash as before.

With some qualities of acetate rayon, additions of swelling agents, such as diethylene glycol, Glyecine A., methylated spirit, etc., exercise a beneficial influence on the penetration of the colouring matter into the fibre, but such bodies must be used with discretion as many of them act also either as delustrants or relustrants, and may produce, therefore, undesired effects. On the

other hand, their use is recommended for Duranol and Dispersol colours in powder, and for other groups of acetate rayon dyestuffs, for the purpose of bringing the dyestuff into a proper state for dispersion in the thickening. Thus with powder brands of the Duranols and Dispersols the printing colour is prepared as below.

20– 60 grms. Duranol or Dispersol dyestuff in powder.
50–100 ,, Glyecine A.
Mix to a fine paste and add—
340–250 c.c. hot water.
Stir for some time and finally stir into—
590 grms. gum Senegal 1 : 1.

1000 grms.

Thereafter the process proceeds as already described.

STEAMING.—In view of the fact that a number of dispersed dyestuffs tend to sublime and to transfer themselves irregularly to adjacent laps of cloth (tech. " mark-off ") in the steamer, it is advisable to steam printed acetate rayon goods between greys, as is customary in the case of certain Alizarin and Chrome colours. In this way any possible damage from sublimation is averted. Another point to note is that cellulose acetate readily loses its lustre at high temperatures in the presence of water, from which it follows that the steaming process should be conducted under conditions as free from moisture as is consistent with the fixation of the colouring matter. In this connection it is highly important to ascertain beyond doubt that no water sprays from pinholes or joints in steam pipes play directly on goods under treatment; such sprays, though too fine to injure other fabrics, are disastrous to cellulose acetate fibres, " blinding " them instantly. These remarks on steaming apply equally to all types of dispersed dyestuffs and to all kinds of acetate rayon, without exception.

Celliton and Celliton Fast Dyestuffs.—These products of the I. G. Farbenindustrie A.G. comprise about forty dyestuffs for printing and embrace the complete colour scale in many variations of shade. In general properties, mode of application, and composition they are similar to the S.R.A., Duranol, and Dispersol series, and most of them are of satisfactory fastness as that quality is understood in acetate rayon dyestuffs. As their name implies, the Celliton Fast colours are the better in this respect; but, with very few exceptions, both groups are of very good fastness to steaming, that is, they do not sublime and " mark off."

The Celliton and Celliton Fast dyestuffs consist of various aminoazo- and hydroxyazo-compounds, aminoanthraquinones, and possibly other organic compounds but, so far as can be ascertained, they embody no new principles differing essentially from those previously established in the S.R.A. and Duranol dyestuffs. Such differences as, at present, exist between the several ranges of acetate rayon specialities are to be sought amongst the similar, but not identical, members of specific groups of dyestuffs that are selected for inclusion in particular ranges of acetate rayon colours, and also amongst the various dispersing agents employed as, for example, ethyl-β-hydroxyethylaniline in the case of Celliton reds. These variations are matters of perhaps important detail, but not of principle, and may be regarded as improvements or otherwise rather than as innovations.

The Celliton and Celliton Fast range includes the following colours for printing:—

A.

Celliton brilliant yellow F.F.
,, yellows 5 G., 3 G.N.
,, printing yellow 3 R.
,, fast pinks R.F., F. 3 B.
,, red violet R.R.
,, fast red violets R.N., R.
,, fast blues B., B.B.

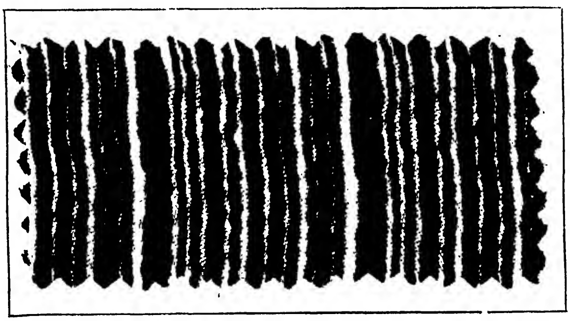
Celliton violet R.
,, discharge violet B.
,, fast violet B.
,, fast blue R.
,, blue extra.
,, blue G.
,, fast blue B.F. conc.

B.

Celliton fast yellows, G., G.R.
,, ,, yellow R.R.
,, orange G.R.
,, red R.
,, scarlet B.
,, fast violet 6 B.
,, fast browns 3 R., 5 R.

Celliton discharge blue 3 R.
,, fast navy blues B.R., B.
,, ,, ,, blue G.T.N.
,, blue 3 G.
,, fast blue green B.
,, fast green B.
,, fast blacks B., G.N., B.T.N.

All the colours under (A) are printed by the recipes given below for the attached pattern.



(I.G.)

Celliton Fast Pink F. 3 B. (25 grms. per Kilo.).
Celliton Fast Blue B. (,, ,,).

(A.)

	Pink	Blue.
Celliton fast pink F. 3 B. pdr. . . .	25 grms.	..
Celliton fast blue B. pdr.	..	25 grms.
Water	100 ,,	100 ,,
Mix to a fine paste and stir into—		
Gum Arabic or Senegal 1 : 1 . .	600 ,,	600 ,,
Glyecine A.	30 ,,	30 ,,
Water	245 ,,	245 ,,
	1000	1000

After printing, the goods are steamed for 20–30 minutes in a cottage steamer, without pressure, using slightly moist steam at 101° C., and afterwards washed and dried. Steaming may also be effected by two passages of 5 minutes each through the rapid ager, but in this case the dyestuffs are not fully developed or fixed. Good results have been obtained by steaming, between greys, in the automatic steaming and ageing machines of Messrs Mather & Platt Ltd.

Dyestuffs under (B) are made up for printing as follows:—

(B.)

{25–100 grms. Celliton or Celliton Fast dyestuff.
{40– 50 ,, Methyl Anon (a proprietary article).

Mix to a fine paste and dilute with—

50–100 grms. water.

Mix well and stir into—

600–500 grms. gum Senegal or Arabic 1 : 1.
285–250 ,, water.

1000

The larger quantity of dyestuff is used for paste colours.

Reducing thickenings for the two recipes are prepared as under:—

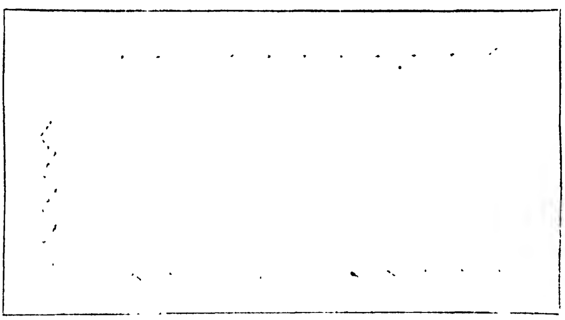
	(A.)	(B.)
Gum thickening 1 : 1	700 grms.	700 grms.
Glyecine A.	20 ,,	..
Methyl Anon	..	30 ,,
Water	280 ,,	270 ,,
	1000	1000

An addition of 5–10 grms. Ludigol per 1000 grms. of printing colour is recommended, as it exerts a favourable effect on the yield; and an addition of Monopol soap promotes levelling.

Sharper outlines are also obtained by adding about 50 c.c. "Red liquor" (aluminium acetate 15° Tw.) to 1000 grms. of printing colour.

Several of the Celliton dyestuffs are dischargeable with Decroline and other similar sulphoxylates and will be mentioned later.

Cibacet Dyestuffs.—The Cibacet colours resemble other acetate rayon dyestuffs in composition and properties. They are very well adapted for printing since they mix perfectly with water alone and disperse in the thickening without settling-out.



Cibacet Yellow G.N. (20 grms. per Kilo.) (S.C.I.B.).

Recipe.

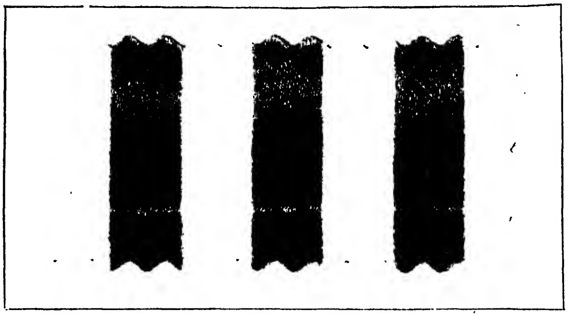
{ 5– 20 grms. Cibacet dyestuff in powder.
{350–380 ,, water (warm).

Mix to a fine suspension and stir into—

645–600 grms. gum Arabic 1 : 1.

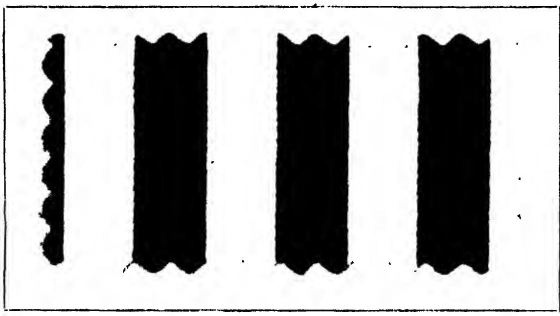
1000

Strain well through fine cloths before printing. The success of these dyestuffs depends on the careful preliminary pasting-up with water.



Cibacet Red 3 B. (20 grms. per Kilo.) (S.C.I.B.).

The foregoing recipe is applicable to all Cibacet dyestuffs.



Cibacet Sapphire Blue G. (20 grms. per Kilo.) (S.C.I.B.).

The printed goods are steamed for ¾ hour between greys, washed, soaped at 50°–60° C. (120°–140° F.) and finally washed and dried.

The Cibacet colours furnish a full range of yellow, orange, scarlet, blue, green, violet, and black shades, all of good fastness to washing and most of them satisfactory to light. A few are dischargeable to a fair white and find a limited outlet in discharge styles.

Setacyl Dyestuffs.—The Setacyl series of acetate rayon dyestuffs (J. R. Geigy, Soc. Anym.) forms a short but more or less complete range of dyestuffs which are soluble in water (with additions), work well in printing, and give very brilliant shades of good fastness to light. Like other dyes of their type they possess no definite affinity for pure cellulose fibres, but on the contrary they are readily fixed on silk and wool, a property which renders them particularly interesting for the printing of level shades on union fabrics of acetate rayon-wool or acetate rayon-real silk mixtures.

The more important members of the group, at the time of writing, are listed below, the numbers in brackets indicating the number of grammes per kilogramme required to give a full shade.

Setacyl printing yellow S. 3 G. conc.	(40).
,, ,, ,, S.G. conc., S.R. conc.	(30).
,, ,, brown S.A.E.	(50).
,, ,, orange S.E. supra.	(40).
,, ,, scarlet S.G.	(30).

Setacyl printing red S.L.		(15).
,, ,, ,, S.B.		(30).
,, ,, violet S.R.D. supra.		(10).
,, ,, greys S.B., S.G.		(20).
,, brilliant blue S.		(25).
,, printing blue B.R.		(20).
,, ,, navy blue B.		(30).
,, ,, black B.L.		(40).

The S. and B. brands are made-up for printing by the following recipes:—

S.

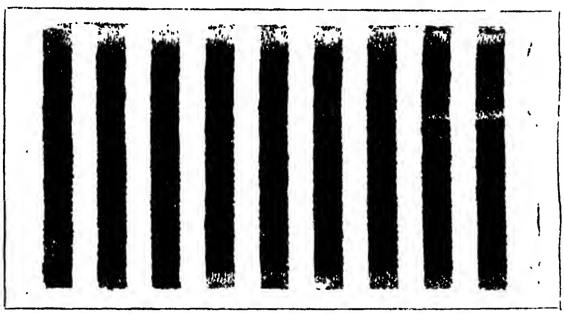
10– 50	grms.	Dyestuff.
40– 40	,,	Dissolving Salt B.
420–380	,,	water.

Dissolve warm and stir into—

500–500	grms.	neutral starch-tragacanth paste.
30 - 30	,,	Irgasol (ethylene glycol monoethyl ether).

Warm to 80°–90°C. and cool before use.

1000



Setacyl Printing Red S.B. (30 grms. per Kilo.) (Geigy).

Special Recipe for Brilliant Blue S.

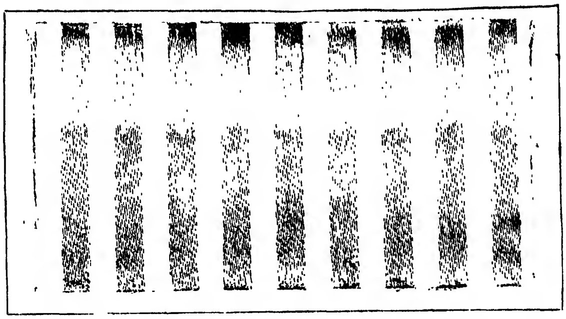
25	grms.	Setacyl brilliant blue S.
320	,,	water.
25	,,	Setacyl salt A.
70	,,	methylated spirit.
30	,,	Irgasol.

Dissolve and add to—

530 grms. thickening.

1000

As thickenings, gum Senegal and gum Arabic are preferable to starch-tragacanth paste, unless the latter contains very little starch. Starch-tragacanth yields a much darker shade, however, and is often used, although it is more difficult to remove from the fibre if the starch content is considerable.



Setacyl Printing Violet S.R.D. Supra (10 grms. per Kilo.) (Geigy).

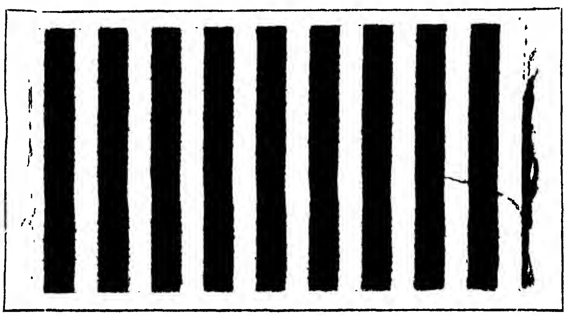
Dyestuffs of the B. brands belong to different groups of colours from those of the S. brands, and are better prepared for printing on the basis of the following recipe :—

B.

20– 40	grms.	dyestuff.
290–270	,,	water.
40	,,	acetic acid 40 per cent.
50	,,	Irgasol.

Dissolve and add warm to—

600	grms.	thickening.
1000		



Setacyl Printing Navy Blue B. (30 grms. per Kilo.) (Geigy).

This last pattern has been printed according to recipe B.

Printing colours prepared as described keep well, and it is advisable to allow them to stand for 12 hours or more before use.

After printing, the goods are steamed for 15 minutes, given an airing, washed, soaped at 30°–40° C. (85°–105° F.), washed, and dried.

The Setacyl colours fix well with the short steaming given and, as they are claimed to be free from the defect of sublimation, no marking off takes place during the steaming process ; nor do the colours mark off or bleed during the subsequent washing and soaping operations.

The S. brands may be mixed together in any proportions and similarly the B. brands, but the two brands interact when mixed together and cannot be so used.

Cellitazol Dyestuffs.—The Cellitazol colours occupy a position between the Ionamines and various dispersed types of dyestuffs, such as the S.R.A. and

Dispersol groups. That is to say, on the one hand the Cellitazols comprise a series of amino- and aminoazo-bases similar to that employed in the manufacture of the Ionamines but, on the other hand, these bases are prepared in such a form as to be readily dispersed in soap solutions and applied to acetate rayon by the same methods as those employed in the application of other dispersed dyestuffs. In short, the Cellitazols yield Ionamine results by means of S.R.A. and Dispersol methods.

All Cellitazol dyestuffs contain at least one primary amino-group and may, therefore, be diazotised and developed on the fibre in the customary manner. They give various shades according to the particular dyestuffs and developers used, some dyestuffs being suitable for only one type of colour, while others give different colours with different developers. Dyed direct, most of the Cellitazols give yellow or orange shades of little interest; it is only when diazotised and developed that they come into consideration for printing purposes, and then only for ground shades in discharge styles. For direct printing, the Cellitazols are of no interest, and even for discharge styles they find but little employment, since they yield very poor whites; their chief use is for the dyeing of black and navy blue on piece goods and yarn and, to a less extent, for cross-dyeing in various shades. Cellitazol A.Z. and Cellitazol S.T.N. are the most important for blacks, and Cellitazol B.N. for blues; Cellitazols R. and R.B. yield shades of yellow, orange, red, crimson, claret, and bordeaux with various developers such as resorcin, β-naphthol, β-oxynaphthoic acid, etc., whilst Cellitazol O.R.B. gives shades of orange, red, and blue similarly. Other members of the Cellitazol group are marketed, and other developers, *e.g.* *m*-phenylenediamine, are used but none finds more than occasional use in this country.

Such Cellitazols as are dischargeable may be printed according to the following recipe:

White Discharge.

200	grms.	Decroline soluble conc.
185	,,	water.
450	,,	British gum 1 : 1.
100	,,	"Kronos" titanium dioxide.
30	,,	Acetine N.
30	,,	Glyecine A.
5	,,	formaldehyde 40 per cent.
1000		

After printing, steam for 5 minutes in the rapid ager, wash and dry.

For ground shades the Cellitazols are dyed in a soap bath (containing 2–3 grms. Marseilles soap per litre) at 170° F., then washed, diazotised, and developed with suitable phenols or amines, washed again and dried.

The "whites" are not very good, and the process is of little practical value.

Damask and Matt Effects on Acetate Rayon.

Damask and matt effects may be produced on acetate rayon fabrics by either mechanical or chemical means, *i.e.* (1) by printing or precipitating insoluble pigments on the fibre, or (2) by local destruction of the lustre by treatment with alkalies and other delustring agents. The latter method is rarely employed for the production of patterned effects owing, partly, to the insufficient contrasts obtained and, partly, to the practical difficulties encountered in the washing-off operations, during which there is a tendency for

the whole body of the goods to be affected and to become, more or less, delustred. On the other hand, treatments in weak alkalies or soap solutions, at or near the boil, are eminently adapted to the production of the so-called dull or matt finishes, so popular at the moment, and for this purpose such treatments are principally employed.

Damask or matt effects were formerly obtained on lustre fabrics by the ordinary method of printing white pigments fixed with albumen. These, while yielding good contrasts, left the material stiff and, moreover, gave a somewhat flat, pasty appearance due to the interstices between the threads being filled up with solid matter to a noticeable extent. A great improvement, as regards mercerised cotton and viscose rayon, was effected by the use of Sericose L.C. dissolved in organic solvents, but unfortunately Sericose L.C. was not applicable to acetate rayon because, being itself a cellulose acetate, its solvents were also solvents for acetate rayon fibres. Latterly there has been brought out, under the name of Opalogen A., a new fixing agent which is free from these drawbacks.

Opalogen A., placed on the market in 1932 by the I. G. Farbenindustrie A.G., is soluble in dilute organic acids, and as its application involves no alteration in the chemical structure of cellulose acetate fibres, it permits of coloured damask effects being produced, at will, by admixture of acetate rayon dyestuffs with the white printing paste.

Damask Effect with Opalogen A. on Acetate Rayon (I.G.).

WHITE DAMASK PRINTING PASTE.

250	grms.	Opalogen A.
500	,,	tragacanth mucilage 65 : 1000.
50	,,	glycollic acid (or lactic acid 50 per cent.).
100	,,	water.
100	,,	China clay.
1000		

Print on unsaponified acetate rayon, dry, steam twice for 5 minutes, each time in the rapid ager, or 10–15 minutes in the cottage steamer without pressure, wash, and dry.

Coloured effects are obtained by adding Indigosols or other suitable dyestuffs to the above printing mixture. Thus—

LIGHT BLUE DAMASK.

50	parts	Indigosol O. 4 B. standard.
950	,,	White damask printing paste (above).
1000		

LIGHT PINK DAMASK.

50 parts	Indigosol pink I.R. extra standard.
950 ,,	White damask printing paste (above).
1000	

INDIGOSOL STANDARDS.

	O. 4 B.	Pink.
Indigosol O. 4 B.	100 grms.	..
Indigosol pink I.R. extra	..	100 grms.
Indigosol Developer G.A.	100 ,,	100 ,,
,, ,, D.	100 ,,	100 ,,
Hot water	700 ,,	700 ,,
	1000 grms. each.	

After printing, the goods are steamed and, *without* washing, developed at 30° C. (85° F.) in a bath of sodium nitrite and sulphuric acid, as described for the printing of Indigosols on acetate rayon (*q.v.*).

The damask effects resulting from these methods of working are very plastic and of good fastness to washing and subsequent dyeing ; the cloth is left in a pliant condition, free from stiffness, and retains the good draping quality so characteristic of acetate rayon fabrics.

Another method of producing matt effects on acetate rayon is based upon the deposition of zinc oxide from solutions of basic zinc chloride applied by padding. Such portions of the material as are desired to remain unaffected (*i.e.* to retain their original lustre) are protected from the action of the zinc chloride by means of mechanical resists such as gum Arabic, gum Senegal, or British gum. The process, known as *lustre printing*, yields brilliant lustred patterns, in white or colours, on a dull matt ground. The method of working is as follows :—

(1) Print white or coloured resists as under :—

	White.	Colours.
Gum Senegal 1 : 1	850 grms.	850 grms.
Glycerine	..	30 ,,
Duranol dyestuff in paste	..	100 ,,
Water	150 ,,	20 ,,
	1000	1000

S.R.A., Celliton, Dispersol, and similar dyestuffs, also Basic and Vat colours, may be used in place of Duranol dyestuffs.

(2) Age or steam as usual for acetate rayon.

(3) Pad at 40°–50° C. (104°–122° F.) straight through the nip of a two-bowl padding machine in a solution of—

1100 c.c. zinc chloride 178° Tw.
125 ,, glycerine.

Add slowly, stirring constantly—

156 c.c. ammonia 25 per cent.
35 ,, water.

(4) After padding, allow the goods to lie for 3–4 minutes and then wash and soap lightly in the open soaper and dry.

During the washing the basic zinc chloride is decomposed with precipitation of zinc hydrate (or oxide) on the fibre and consequent blinding of its lustrous sheen on the parts left unprotected by the printed gum resists.

Basic zinc chloride solutions prepared as described are somewhat unstable, particularly in the cold, and are better made up as required.

It may be noted here that damask effects on viscose rayon may be obtained by any of the ordinary methods of printing pigments using zinc oxide, china clay, blanc fixe, or titanium oxide as filling agents. Sericose L.C. extra produces exceptionally good results as a fixing agent, and may, moreover, be employed in place of albumen for thickening and fixing pigments and bronze powders in ordinary printing on cotton, etc., when dissolved in Sericosol N. and methylated spirit. The solvents are volatile and the goods require no steaming for fixation as when albumen is used, the Sericose L.C. being left in an insoluble state on the fibre and so holding any pigment incorporated with it.

WHITE DAMASK ON VISCOSE RAYON.

200	grms.	titanium dioxide (Kronos).
100	,,	methylated spirit 95 per cent.
200	,,	solvent mixture (below).
500	,,	Sericose solution.
1000		

SERICOSE SOLUTION.

100	grms.	Sericose L.C. extra (acetyl cellulose).
900	,,	Solvent mixture.

Stir cold until dissolved.

1000

SOLVENT MIXTURE.

400	grms.	Sericosol N.
300	,,	methylated spirit 95 per cent.

Sericosol N. (an improved brand of Sericosol) is a neutral, colourless, odourless liquid, highly volatile and possessing no irritating physiological effects.

After printing, the goods are merely dried and, if necessary, calendered.

Any pigment may be used in paste or powder form. Paste pigments with a high water content are apt to cause gelatinisation of the printing colour on standing. In such cases the printing colour is warmed slightly, then regaining its normal consistency.

PRINTING OF UNION FABRICS.

(Rayon + Other Fibres.)

A large proportion of the Art Silk fabrics, as they are called, that are used for printing purposes, consists of mixtures of regenerated cellulose rayons and cellulose acetate rayons with each other, and with cotton, natural silk, and wool—mixtures which demand not always complex, but usually some special, treatment for their colouring. It is impossible to deal in full with all the contingencies and problems that are likely to arise in connection with the printing of these diverse materials, but the following *résumé* of the general principles applied in practice will give a fair idea of the usual lines of approach.

(*a*) **Viscose/Cotton Fabrics.**—Apart from careful mechanical handling, mixed goods of this description are dealt with as if they were pure cotton, and any of the colouring matters and processes used for that fibre and suitable at the same time for printing viscose rayon (*q.v.*) are applicable without modification.

(*b*) **Viscose/Natural Silk Fabrics.**—For these, the Basic and Chrome colours

are largely employed according to the recipes used for cotton, but preferably containing a little extra acetic or formic acid. For faster work the Vat colours and Indigosols come into consideration. The Direct dyestuffs also find occasional use; they are made up with sodium phosphate, as for cotton, and acidified with acetic acid in order to facilitate their fixation on the silk. After printing, the goods are steamed and after-treated according to the methods appropriate to the dyestuffs employed.

(*c*) **Viscose/Wool Fabrics.**—Mixtures of these fibres may be dealt with as already described under the printing of half-wool. The details given for the printing of Indigosols on wool are equally adapted to the printing of viscose/wool unions.

The Acid azo colours are not used in these styles.

(*d*) **Acetate Rayon (Celanese, etc.)/Cotton; Acetate Rayon/Viscose Fabrics.**—All mixtures of acetate rayon with cotton or regenerated cellulose rayon may be regarded as one and the same thing so far as colouring is concerned. These fabrics, and incidentally, those consisting of cellulose acetate and wool or silk, present more difficulty in printing than does any other type of textile material. Owing to the different affinities of the constituent fibres for the same dyestuffs, it is by no means easy to produce solid shades of consistent fastness and brightness on each fibre unless some compromise is made. Thus, in the case of the acetate rayon/cotton mixtures under review, if it be desired to print Vat colours, which yield level solid shades, these must be applied in alkaline media and some loss of lustre must be expected; the alkalinity of the printing colour saponifies those portions of the acetate rayon with which it comes into contact and converts them, more or less, into cellulose. The printed parts of the fabric no longer consist of acetate rayon alone, but are covered by a layer of cellulose which, in heavy patterns, is often recognisable in daylight by a marked diminution of gloss. The same effect is produced by the Direct dyestuffs which require an addition of caustic soda to the printing colour in order to confer the necessary affinity on the acetate rayon by partial saponification.

The only dyestuffs which give solid shades, without saponification, on acetate rayon/cotton material are Basic and Indigosol colours, a few Chrome colours of the Gallocyanine group, Diphenyl black, and the oxidation browns. These are printed by the methods already described for pure acetate rayon, the Basic and Chrome colours requiring only an addition of the necessary mordants—tannic acid and chromium acetate—to enable them to fix on the cotton or viscose threads of the union goods. The printing colours used for cotton, thickened with gums, may be used with safety, the various appropriate steamings and after-treatments being carried out in the usual manner.

With the exception of the Indigosols or Soledons, none of these colours is fully satisfactory. The Basic colours are brilliant but loose; the Chrome colours are extremely limited in range, being restricted to dark blues and greys; the shades of the oxidation browns are little in demand; Diphenyl black is useful for single-colour patterns, but is useless for close-fitting outlines as it is easily prevented from developing; and the Vat and Direct colours, though largely used, and satisfactorily so, suffer from a tendency to impair the sheen of the fabric.

The Indigosols and the Soledons, on the other hand, may be employed with confidence for any styles to which they are adapted on 100 per cent. acetate rayon, the printing processes being exactly the same as those described for that material (*q.v.*). They fix on both fibres equally well, and give ranges of bright shades of great all-round fastness. But they are somewhat expensive in cost of production, and the fastest work, therefore, is usually executed in Vat colours which, after all, when carefully used, leave little to be desired.

For commoner classes of work, where extreme brightness of shade is a *sine qua non*, the Basic dyestuffs hold first place. If possible, however, their use is to be avoided; they are moderately fast to washing, but fugitive to light, and fade to horrible shades.

Another, and very useful, method of obtaining solid shades on union goods is a combination of acetate rayon and cotton processes. Advantage is taken of the fact that Duranol, Dispersol, S.R.A., and other dispersed dyestuffs may be mixed with ordinary Direct dyestuffs in any proportion without fear of interaction. The Duranol colour selected for the acetate rayon must be matched with a Direct dyestuff (for the cotton), which not only must have no affinity for acetate rayon, but must not even stain it. There are many dyestuffs of this kind, amongst the best known being the C.R. Chlorazol colours of the Imperial Chemical Industries, Ltd. By matching any one of these, or a mixture of them, with a suitable Duranol dyestuff, and combining the two in a single printing colour, it is easily possible to obtain a great variety of solid shades on mixed fabrics of acetate rayon and cotton or viscose rayon. The Direct dyestuff fixes only on the *pure* cellulose threads, whilst the Duranol dyestuff fixes only on the cellulose acetate threads, neither staining the other fibre in any way. For example, a solid violet may be obtained from the following mixture :—

VIOLET.

10 grms. C.R. Chlorazol fast pink B.K.S.
5 ,, C.R. Chlorazol fast helio B.K.S.
50 ,, glycerine.
310 ,, water.
Dissolve and add—
600 grms. British gum 1 : 1, or gum Senegal 1 : 1.
Warm together, cool, and add—
25 grms. Duranol violet 2 R.S. 200 paste fine.

1000

Similarly a solid pink is obtained by using a mixture of—

PINK.

25 grms. Duranol red 2 B.S. 200 paste fine.
15 ,, C.R. Chlorazol fast pink B.K.S.

And an orange from—

ORANGE.

25 grms. Duranol orange G. 200 paste fine.
15 ,, C.R. Chlorazol fast orange A.G.S.

The goods, after printing, are steamed for one hour at 100° C. (212° F.) without pressure in fairly dry steam, washed in running water, and dried. The loosely adhering dyestuffs are easily removed from the fibres for which they have no affinity and, provided that there is a copious supply of cold wash water, there is no staining of the white ground.

"*Shot*" *Effects* in contrasting shades are obtained by a simple variation of the foregoing process, namely, by printing mixtures of Duranol and Direct dyestuffs of different colours instead of matched colours. After steaming and thorough washing, the acetate rayon fibres will appear of one colour, whereas the cotton, silk, or wool fibres will be of another.

EXAMPLES OF SHOT EFFECTS.

Union fabric printed with—	Cotton, etc.	Acetate Rayon.
(1) Duranol red 2 B.S. 200 paste fine; C.R. Chlorazol sky blue F.F.S.	Blue	Bluish-red
(2) Duranol red G. 200 paste fine; C.R Chlorazol sky blue F.F.S.; ,, ,, fast yellow F.G.S.	Bright green	Red
(3) Duranol orange G. 200 paste fine; C.R. Chlorazol sky blue F.F.S.	Blue	Orange
(4) Duranol violet 2 R.S. 200 paste fine; C.R. Chlorazol fast yellow F.G.S.	Yellow	Purple
Or, omitting one component—		
(5) Duranol brilliant blue G.S. paste fine	White	Blue
(6) C.R. Chlorazol fast red K.S.	Red	White

Various other combinations are obviously possible, and any other types of Direct dyestuffs and acetate rayon dispersed colours may be utilised for their production.

"Shot" effects of this description are occasionally printed as blotches, or in heavy single-colour patterns as novelties, but they are not in much demand and are more popular in dyed goods than in prints. Still they are interesting as illustrations of the possibilities inherent in combinations of different dyestuffs and different textile fibres, and as such they merit mention.

(*e*) **Acetate Rayon/Silk Fabrics.** — The Basic, Chrome mordant, Vat, and Indigosol dyestuffs are all applicable to these unions by the methods employed for cotton or silk.

In the case of the Vat colours the alkali must be potassium carbonate, and as little of it must be used as suffices to enable the dyestuff to be properly reduced and fixed without tendering the natural silk.

The Indigosols are best printed according to the wet-developing processes described under "Silk and Half-Silk Printing."

The Direct dyestuffs cannot be used alone for printing solid shades on acetate rayon/silk goods owing to the necessity for the addition of caustic soda to the printing pastes in order to obtain fixation on the cellulose acetate fibres. Fairly good results have been obtained with soda-ash as saponifying agent for these fibres, but even this is not entirely satisfactory, as the natural silk fibre is still liable to be damaged, in steaming, at the concentration of soda required to bring about full fixation on the cellulose acetate fibre, and the acetate fibre itself is also liable to loss of lustre.

In conjunction with Duranol colours, however, the Direct dyestuffs behave in the same way as on acetate rayon/cotton goods, and may be used in precisely the same manner for printing either solid shades or "shot" effects.

Amongst acetate rayon specialities the Setacyl dyestuffs of Messrs J. R. Geigy, Soc. An., Bâle, are of outstanding interest to the printer of rayon fabrics, since they are equally applicable, by a common process, to natural silk, wool, and acetate rayon and, consequently, they give solid, level shades on various mixtures of these fibres. A description of these colours, together with particulars of their application and printed patterns, has already been given under "Printing of Acetate Rayon Dyestuffs."

(*f*) **Acetate Rayon/Wool Fabrics.**—In the main, the printing of goods

of this type follows closely on the lines just indicated for acetate rayon/silk materials.

The Basic dyestuffs, having a definite affinity for both fibres, may be printed either with or without tannic acid to yield solid shades. An addition of tannic acid to the printing colour, followed by fixation in a bath of tartar emetic after steaming, however, improves the fastness to washing but, otherwise, has little effect on the general fastness.

Chrome colours of the Gallocyanine group are applied in the manner customary for cellulose acetate goods, and must, of course, contain the necessary amount of mordant, in the form of chromium acetate, in order to obtain complete fixation on the woollen portion of the cloth.

The Setacyl dyestuffs, as previously noted, give the same shades on wool as on acetate rayon, and call for no further description.

The Direct dyestuffs alone are not suitable for the production of solid shades for the reasons adduced under printing of Acetate Rayon/Silk Mixtures. But in admixture with Duranol, Dispersol, Celliton, Cibacet, or S.R.A. colours they are largely used for this purpose, according to the methods already given (see Acetate Rayon/Cotton Fabrics). The Direct colours are faster on wool than on cotton.

Neither the ordinary Vat dyestuffs nor the Indigosols find much employment in the printing of acetate rayon/wool mixtures. If it be desired to make use of them for the sake of fastness, they may be printed by the methods in current use for wool and acetate rayon, respectively, *e.g.* the Vat colours by the Rongalite-potash processes described for wool; the Indigosols by the nitrite, chlorate, or lead chromate wet-developing processes, described elsewhere for acetate rayon and wool. The two last-mentioned processes give the best results.

Woollen fabrics figured with ornamental woven motifs in acetate rayon may be printed or dyed in two contrasting colours simultaneously by relying on the characteristic affinities of Direct, Acid, and Duranol dyestuffs for the two constituent fibres of the material. The methods employed are identical with those already dealt with in connection with acetate rayon mixtures with other fibres, viz. "shot" effects with combinations of Duranol and C.R. Chlorazol dyestuffs. Similarly, the acetate rayon may be left uncoloured by printing only a Direct or an Acid colour which fixes on the wool alone, leaving a white pattern of rayon on a coloured ground; or the reverse effect, a coloured rayon pattern on a white woollen ground, may be obtained by printing or dyeing a Duranol, Celliton, or S.R.A. dyestuff, which has no affinity for wool and fixes only on cellulose acetate. Some of these acetate rayon dyestuffs stain wool rather badly, and a careful selection has to be made to ensure clean whites. Fancy styles of this kind are principally in demand for furnishing fabrics—draperies, cushion covers, and upholstery goods—and do not constitute a very important branch of printing.

RESIST STYLES ON ACETATE RAYON.

Although resist styles, in general, are not applicable to acetate rayon fabrics, owing to the lack of suitable dyestuffs, the complexity of the suggested processes and the difficulty of handling the goods in a manner adequate to the production of clean whites and bright colours, it is, nevertheless, possible to reproduce the effects of the most important of them—the classic Aniline black style—by a method evolved by the I.G. Farbenindustrie A.G.

The Prud'homme Aniline black resist process itself cannot be operated satisfactorily on unsaponified acetate rayon, but by using Diphenyl black

base and *p*-phenylenediamine with Celliton colours as reserves, an analogous process is rendered available for acetate rayon—a process which yields white and coloured resists on black and brown grounds, fully equal to the Aniline black styles on cotton. The colours are fast to washing, and neither the lustre nor other properties of the acetate rayon are impaired in any way.

The following resists are printed on 100 per cent. acetate rayon cloth:—

WHITE RESIST.

50	grms.	Rongalite C.
70	,,	water.
580	,,	B.W.C. thickening (below).
150	,,	Decroline soluble conc.[1]
150	,,	sodium acetate.
1000		

COLOURED RESISTS.

80–100	grms.	Celliton or Celliton Fast dyestuff in paste.
110–90	,,	water.
60	,,	Glyecine A.
450	,,	British gum thickening 1 : 1.
60–200	,,	zinc oxide 50 per cent. paste.
240–100	,,	sodium acetate.
1000		

B.W.C. THICKENING.

60	grms.	wheat starch.
200	,,	water.
300	,,	British gum thickening 1 : 1.
200	,,	China clay.
240	,,	water.
1000		

Boil and cool.

After printing and drying thoroughly, at not too high a temperature, the goods are padded with Diphenyl black or Paraphenylenediamine brown. In order to prevent the formation of halos around the printed colours, the cloth must be padded, "straight through the nip," between the bowls of a two-bowl padding mangle, the lower bowl being partly immersed in the padding liquor, as is usual for Aniline black resist styles.

DIPHENYL BLACK PADDING LIQUOR.

(A.)

40	grms.	Diphenyl black base I. (I.G.).
50	,,	lactic acid 50 per cent.
130	,,	acetic acid 50 per cent.
		Dissolve by heat and stir into—
100	grms.	tragacanth mucilage 65 : 1000.
100	,,	water.
		Mix well and make up with—
80	grms.	water, to
500		

Cool before use.

[1] Decroline soluble conc. is a neutral formaldehyde-sulphoxylate of zinc.

(B.)
30 grms. sodium chlorate.
100 „ water.
25 „ aluminium chloride 53° Tw.
4 „ cupric chloride 77° Tw.
331 „ water.
10 „ turpentine.

500

For use:—500 grms. (A.).
500 „ (B.).

PARAPHENYLENEDIAMINE PADDING LIQUOR.

20 grms. Paraphenylenediamine.
300 „ boiling water.

Dissolve and add—

430 grms. cold water.
2 „ Rongalite C.
8 „ water.
100 „ sodium chlorate solution 20 per cent.
100 „ ammonium chloride solution 20 per cent.
20 „ tartar emetic-glycerine solution.
20 „ ammonium vanadate 1 : 1000.

1000

TARTAR EMETIC-GLYCERINE SOLUTION.

40 grms. tartar emetic.
620 „ water.
340 „ glycerine.

1000

The padded goods pass directly over a cylinder drying machine, and are then steamed for 5–6 minutes in the rapid ager, passed through a cold bath of bichromate of soda, soured with acetic acid, washed, soaped at 70° C. (160° F.), washed, and dried. Care must be taken to avoid over-chroming Diphenyl blacks, as they are liable to turn brownish if over-oxidised.

Duranol, S.R.A., and other similar dyestuffs may be used in this process; and Fuscamine may be employed to replace, either wholly or in part, *p*-phenylenediamine, for the production of lighter and yellower browns.

Excellent whites have been obtained under the foregoing black and brown pads by means of the sulphite type of resist used so largely in the corresponding styles on cotton.

WHITE RESIST.

250 grms. potassium sulphite 90° Tw.
100 „ zinc oxide.
250 „ water.
250 „ British gum powder.

Boil and add—

150 grms. sodium acetate.

1000

Cool before use.

The following dyestuffs are indicated for bright resist colours :—

Celliton fast blue B. paste.	Duranol brilliant blue C.B.S. paste.
,, ,, yellow G. paste.	,, blue R. paste.
,, ,, pink F. 3 B. paste	,, orange G. 200 paste fine.
,, ,, red violet R.N. paste.	,, red G.S. 200 paste fine.
,, blue, extra paste.	,, light yellow S. 200 paste fine.
,, red R. paste.	,, violet 2 R.S. 200 paste fine.

etc.

Bright greens are obtained by mixing yellows and blues in various proportions, thus :—

80 grms. Celliton fast yellow G. paste } per 1000 grms. of printing colour.
20 ,, ,, ,, blue B. paste }

And similarly for other compound shades.

Reserves under Vat Colour Grounds.—Processes depending on the use of chlorates, non-volatile organic acids, Ludigol, and the Leucotropes, have been proposed, from time to time, for the production of resist or reserve effects under subsequently printed grounds (machine pads) of Vat colours on acetate rayon. These various processes are derived from analogous methods employed largely in cotton printing, and while some of them have given encouraging results in bulk trials, none of them appears to have passed beyond the experimental stage ; at any rate no particulars of a really reliable process are available. But the ideas embodied, applied to Duranol, Celliton, S.R.A. colours, etc., are suggestive, and probably feasible, and well worth the attention of printers dealing with unsaponified acetate rayon styles.

DISCHARGE STYLES ON ACETATE RAYON.

These styles fall into two distinct and sharply defined groups, viz.—

(A.) Discharges on unsaponified acetate rayon,
(B.) Discharges on saponified acetate rayon,

these having little in common except that hydrosulphites are used as discharging agents in both cases.

(A.) Discharges on Unsaponified Acetate Rayon.

Up to the present no reliable process has been devised for the production of *permanent* white discharges on fabrics composed of pure unsaponified cellulose acetate. White discharges which at first appear to be perfectly satisfactory almost invariably undergo a change of hue during storage, generally in a very short time, and become yellowish or brownish in shade or take on a very pale tint of the ground colour. Coloured discharges are modified in the same way, though the effects are much less noticeable and are relatively unimportant except in the case of light blues and violets, which often lose considerably in purity.

These difficulties are due in part to the impermeability of cellulose acetate fibres, which prevents the discharging agents from penetrating sufficiently deeply into the body of the dyed material to exercise their full effect on the ground shade ; but the chief cause of " bad whites " is that the reduction and decomposition products of the discharged portions of the ground shade are retained tenaciously by the cellulose acetate fibres and cannot, by any practicable means, be washed out completely from them. The residual decomposition products of dischargeable acetate rayon dyestuffs, left on the

fibre, consist of amino compounds, and in the case of Basic dyestuffs, leuco compounds of the colouring matter. These bodies re-oxidise in storage, the amino compounds forming pale yellow or brown products of the Paraphenylene-diamine brown type, and the leuco compounds being re-converted into pale shades of the original dyestuffs, thus destroying the purity of the white. The difficulty is physical rather than chemical, for if only the residual products, held in solid solution by the fibre, could be completely eliminated by a vigorous washing or soaping at a sufficiently high temperature, the problem would be solved. Unfortunately this is out of the question, as the lustre of cellulose acetate rayon is destroyed at high temperatures.

Improved results, however, may be obtained by additions of various swelling agents to the discharge printing pastes. In this connection the Imperial Chemical Industries, Ltd., have patented the use of metallic sulpho-cyanides (E.P. 262254) which possess the property of swelling the cellulose acetate fibre, and thereby permit of the more or less complete penetration of the discharge pastes into the body of the fabric, with a corresponding improvement in the quality of the discharge white. It is claimed, also, that the use of calcium or zinc sulphocyanide facilitates the removal of the decomposition products even to the point of complete elimination, but this claim, while apparently justified in some instances, is subject to many exceptions and must be accepted with reservations. The amount of sulphocyanide to use for either white or Basic colour discharges varies between 100 and 150 grms. per kilogramme of printing colour, according to the depth of the ground shade to be discharged. The process has no detrimental effect on the appearance or strength of the material, and it is, up to the present, the best method to employ for the production of discharge effects on all piece goods containing unsaponified acetate rayon.

Apart from the question of indifferent whites, the development of fast discharge styles on acetate rayon has been hampered, to a great extent, by the limited number of ground shades capable of being discharged. Numerous dyestuffs are certainly available for this purpose, but, as indicated in the following list, they consist, in the main, of yellows, oranges, and reds, many of which are either identical or approach each other so closely in shade as to afford very little variety. In addition, there are a few reddish-browns and reddish-violets, and several blues and greens, which are suited only for discharges in colour—not white. The range is particularly weak in fast blues, greens, and violets, and contains practically none of the important group of homogeneous tertiary shades which are so valuable a feature in the dyestuff ranges used for other fibres.

Working Methods.—The undermentioned list of dyestuffs contains the more important members of the various series suitable for dyeing dischargeable ground shades on unsaponified acetate rayon :—

Yellows.

Dispersol fast yellow A.S.
* ,, yellow 3 G.S.
Cibacet yellow G.N.
Celliton fast yellow G.R.
,, ,, ,, G.
,, yellow 5 G.
Cellit fast yellow G.G.N.
,, ,, ,, R.
Metanil yellow Y.K.S. (acid).

Oranges.

Ionamine B.S. (dyed direct).
Chlorazol fast orange G.S. (unique example).
Dispersol fast orange B.S.
* ,, ,, ,, A.S.
Cibacet orange 2 R.
* Cellit fast orange G.
* Naphthalene orange G.S.
* ,, ,, IV.K.S.
S.R.A. fast golden orange I.

REDS.

Dispersol fast red A.S.
,, red R.S.
,, fast scarlet B.S.
,, ,, crimson B.S.
Cibacet red G.R.
,, scarlet G.
Celliton red R.
Cellit fast red B.B.
,, ,, rubine B.
,, ,, red B.
Ionamine G.A.S. (direct-dyed).
,, red K.A.S.
* Coomassie red G.S. (acid dye).
Magenta (basic dyestuff).
S.R.A. reds I., III., V.
Setacyl scarlets G., 2 G.
,, reds G., B., V.

VIOLETS.

* Cellit violet R.R.
,, fast violet 4 R.
Celliton red violet R.R.

ORANGES (*cont.*).

S.R.A. fast golden orange III.
,, orange I.
,, ,, III.
Setacyl direct orange G.
,, ,, ,, 2 R.

BLUES.

* Cibacet turquoise blue.
Cellit blue R.
* Turquoise blue G.S. (basic dye).
* Acronol brilliant blue A.S. (basic dye).
* Setocyanine (basic dye).
* Setoglaucine (basic dye).
S.R.A. discharge blue A.

GREENS.

* Malachite green (basic dye).
Acronol green B.S. (basic dye).

BROWNS.

Dispersol fast brown 4 R.S.
Celliton fast brown 3 R.
,, ,, brown 5 R.
* Cellit brown G.

MISCELLANEOUS.

Dispersol diazo black A.S. (developed β-oxynaphthoic acid).
Ionamine black A.S. (direct-dyed).
* ,, ,, ,, (developed β-oxynaphthoic acid).
* ,, B.S. (developed β-oxynaphthoic acid).
* ,, B.S. (developed β-naphthol).
* ,, G.A.S. (developed β-naphthol).
* ,, M.A.S. (direct-dyed; developed β-naphthol).
* Cellitazol A.Z. (diazotised and developed black).
* Citronine Y.S. (acid dyestuff).

None of the Duranol dyestuffs is dischargeable.

Dyestuffs marked * are suitable for coloured discharges only, good white discharges not being obtainable.

The goods are dyed in different manners according to the type of dyestuff employed.

The **Ionamines** are dyed in a slightly acid or alkaline bath; 1 per cent. (on cloth weight) of formic acid or soda-ash is generally used as assistant. Those which are to be developed are diazotised, after dyeing, in the usual manner with sodium nitrite and developed with the appropriate developer according to the procedure usually followed for these operations.

Dispersed dyestuffs are mixed, or pasted if in powder form, with water at 40°–50° C. (105°–120° F.) and, after further dilution with condensed water, are filtered through a fine-meshed sieve or cloth into the dye bath at 50° C., the bath containing 2–3 parts Marseilles soap, soluble oil, etc., per 1000 parts dye liquor. Dyeing is carried out at 60°–75° C. (140°–167° F.) for $\frac{3}{4}$–1 hour in the usual manner. **Dispersol diazo black A.S., Cellitazol A.Z. and similar**

dyestuffs are diazotised with 2–3 per cent. sodium nitrite and developed with 4–5 per cent. β-oxynaphthoic acid at 55°–65° C. (130°–150° F.) for ½–¾ hour.

Basic dyestuffs are dyed at 65° C. (150° F.) from a bath containing 1–2 per cent. acetic acid on the weight of the cloth and from 5 to 20 grms. of magnesium chloride per litre of dye liquor. The temperature of dyeing is gradually raised during 15–20 minutes to 65° C., and maintained at this point for ¾ hour longer, after which the goods are washed off in dilute acetic acid, washed in water and dried.

The **Acid dyestuffs** are rarely used now that so many newer products are available. They may be dyed from a soap bath charged with 2–3 per cent. Marseilles soap, Monopol Brilliant Oil or soluble oil, then washed and dried.

The goods, dyed by any of the foregoing methods, are printed with one or other of the discharge pastes detailed below.

WHITE DISCHARGES ON ACETATE RAYON.

	I.	II.	III.	IV.
Formosul (Brotherton)	100–300	..	..	..
Decroline sol. conc. (I.G.)	..	150–200	250	..
Hydrosulphite B.Z. sol. (S.C.I.B.)	..	..	..	250
Water	250– 80	265–215	200	..
British gum thickening 1 : 1	550–400	550	500	600
Diethylene glycol	0–120	..	..	..
Zinc sulphocyanide, or Calcium sulphocyanide 88° Tw.	100	..	..	..
Acetine	..	30	..	..
Glyecine A. or Fibrit D.	..	..	50	..
Formaldehyde 40 per cent.	..	5	..	..
Tartaric acid	..	..	..	50
Water	..	..	..	100
	1000 parts each.			

Recipe I. of the Imperial Chemical Industries, Ltd., is the best recipe for general purposes and may be relied upon to give as good results as are possible in these styles. Recipes II. and III. are recommended for Celliton and Cellitazol dyestuffs, and recipe IV. for Cibacet dyestuffs, but their uses are covered by recipe I. Decroline soluble conc. and Hydrosulphite B.Z. soluble are both zinc salts of formaldehyde-sulphoxylic acid.

A common practice, employed for the purpose of imparting temporary brilliancy to white discharges, is to load the printing colour with zinc oxide, China clay, blanc fixe, titanium oxide, and other white plastic substances. These are effective, for a time, in masking any shortcomings in the discharge, but eventually they wash off and leave the white in the condition it would have been had they not been used.

An addition of anthraquinone paste or of Leucotrope W. to white discharge printing pastes is often beneficial in promoting a more perfect discharge, and facilitates also the more complete removal of decomposition products.

In view of the powerful reducing action of concentrated formaldehyde-sulphoxylate discharge colours it is highly advisable to pad the dyed cloth, before printing, with Ludigol or sodium chlorate solution, or Resist Salt L., as recommended elsewhere for the prevention of "scumming."

Coloured discharges may be, and usually are, obtained with the Basic dyestuffs normally employed in hydrosulphite discharge styles (*q.v.*).

BASIC COLOUR DISCHARGES (General Recipe).

30	grms.	Basic dyestuff.
50	,,	methylated spirit.
50	,,	phenol or resorcin.
200	,,	gum Arabic 1 : 1, or British gum 1 : 1.
200	,,	gum Arabic 1 : 1 (or British gum 1 : 1).
250	,,	Hydrosulphite B.Z. (water-soluble).
60	,,	tannic acid.
50	,,	tartaric acid.
110	,,	water.
1000		

For coloured discharge effects fast to light and soaping the Vat dyestuffs are utilised. They are applied by the standard Rongalite-potash processes, supplemented by additional amounts of Rongalite or Formosul as required for discharging particular ground shades.

After printing with the foregoing white and coloured discharges, the goods are steamed for 5–6 minutes in the rapid ager, in air-free steam, and then, if they contain white discharges only, they are simply washed thoroughly and dried. In the case of Basic colour discharges, the steamed goods are run, in an open soaping range, through (1) a small tank of water, (2) a bath of tartar emetic, (3) and (4) washing tanks, and finally dried over steam-heated cylinders. Some Basic dyestuffs form leuco compounds during steaming, and these, if not completely re-oxidised in the washing operations, may be fully developed subsequently by a passage through sodium perborate or bichromate solutions.

Vat colour discharges are steamed for 5–6 minutes in the rapid ager, washed lightly, chromed, washed, soaped at 50°–60° C., washed, and dried.

If preferred, Basic colour discharges may be printed *without* tannic acid, phenol, and resorcin, the dyed cloth in this case being previously padded in tannic acid or Katanol O.N., according to the process used for cotton.

Union fabrics of acetate rayon with cotton or viscose are more frequently dealt with by the Saponification process than by the methods just described. But, where the ground shades are such as can be dyed on unsaponified acetate rayon with dispersed dyestuffs, it is often more convenient and more expeditious to dye unions of this kind with combinations of dispersed and Direct dyestuffs which may be worked together without reacting on each other. Two methods may be employed, viz. (*a*) the one-bath process, or (*b*) the two-bath process (in which the constituent fibres are dyed separately). If the dyestuffs are matched, the result is a solid shade on the mixed fabric; if they are of contrasting or different colours, the result is a "shot" or "two-tone" effect. As there is nothing to choose between the two methods, the one-bath process is the more popular and is most generally used in practice for obvious reasons.

Taking Dispersol and C.R. Chlorazol dyestuffs to represent acetate rayon dyestuffs and Direct dyestuffs respectively, the general procedure of dyeing is as follows: The Dispersol colour is diluted with water and sieved into the warm dye bath (50° C.); the C.R. Chlorazol colour, previously dissolved in water, is then added, together with Glauber's salt or common salt as required. The cloth is entered and the temperature is gradually raised to 77° C. (170° F.) and the dyeing continued at this temperature for ¾ hour. Soluble oil or soap

may be added to the dye bath, if desired, to increase penetration, and further additions of Glauber's salt may also be made in order to exhaust the Chlorazol dyestuff; such additions do not affect the exhaustion of the Dispersol dyestuff, but, in the presence of soap or soluble oil, must be made with discretion, otherwise the latter may be salted out.

After dyeing the goods are well washed, dried, prepared in Resist Salt L., or Ludigol, printed with the discharges given earlier in this section and, thereafter, after-treated as described for pure acetate rayon fabrics.

Some of the "shot" and "two-tone" effects, when dyed on weaves that show up the contrasting colours to advantage, give very attractive discharge prints, but, for some subtle reason, they have, hitherto, failed to appeal to the public, and they are much less in demand than similar styles on plain uniform ground shades.

(B.) Discharges on Saponified Acetate Rayon.

Although the saponification process has fallen into almost complete disuse for the dyeing of plain shades, it still retains its importance in the printing of discharge styles, and especially so for those which are produced on fabrics composed of mixtures of acetate rayon with mercerised or unmercerised cotton.

As already noted, cellulose acetates are converted into cellulose when treated with alkalies, and if the conversion is carried to completion they lose their intrinsic properties altogether and, at the same time, acquire the same dyeing properties as cotton. These results are obtained to a less degree by partial conversion, the increased affinity for cotton dyestuffs and the loss in weight, tenacity, and lustre being proportional to the amount of alkali consumed in removing acetyl groups.

Partial conversion of cellulose acetate into cellulose constitutes the process of Saponification as understood in the printing and dyeing trades. The process is subject to some irregularities and, naturally, the properties of acetate rayon are modified considerably by the treatment, the gloss in particular suffering if the saponification proceeds too far, though peculiarly enough the characteristic handle of the material appears to be little affected. These drawbacks, however, are more than counterbalanced by the invaluable advantage of being able to dye acetate rayon with easily dischargeable Direct cotton colours, and thus bring it into line with cotton and viscose rayon materials for the production of ground shades which cannot be dyed and discharged satisfactorily on unsaponified cellulose acetate goods.

For all discharge styles on goods consisting of acetate rayon, or its mixtures with cotton and viscose, the saponification process is most convenient and much more comprehensive than that depending on the use of special acetate rayon dyestuffs. It enables any desired shade to be dyed and discharged with ease and certainty; less concentrated discharging agents may be used, with correspondingly less risk of damage from "scumming"; and the final results are fully equal to those obtained on other cellulose fibres.

The objective of saponification is to form a sufficiently thick layer of regenerated cellulose on the surface of the cellulose acetate fibres to endow them with an affinity for Direct dyestuffs without, at the same time, depriving them unduly of their gloss and tenacity. These conditions may be attained by saponifying acetate rayon with about 10 per cent. of its weight of caustic soda at 75° C. for $\frac{1}{2}$–$\frac{3}{4}$ hour in a dye beck containing 100 times its weight of water. Milk of lime and salts with an alkaline reaction, such as, for example, soda-ash, potassium carbonate, silicates, aluminates, and acetate

of soda may be used in place of caustic soda for saponification, but, with the exception of soda-ash and potassium carbonate, they are rarely employed.

In order to avoid prolonged treatment in dye becks, to increase the rate of production and to ensure the utmost possible regularity in the results, the process of saponification is usually carried out, in print works, on padding mangles and steam-heated drying cylinders.

The mangles used are of the ordinary 3-bowl type—one brass bowl between two rubber bowls—and are arranged to give two immersions and two expressions (or 2 dips–2 nips).

The cylinders of the attached drying machine are divided up into three separate sets or "stacks," each with its own steam supply, and so regulated that the padded cloth is dried in three stages of increasing temperature. In this manner the alkaline liquor is allowed sufficient time to react with the cellulose acetate, and the degree and duration of the saponification can be controlled, at will, by varying the running speed of the padding mangle or the temperature of the drying cylinders.

The saponifying liquors most commonly used in padding machines consist essentially of solutions of caustic soda or potassium carbonate, to which may be added varying proportions of methylated spirit in order to bring about more thorough penetration of the goods, and of glycerine, glucose, and other softening agents for the purpose of keeping the cloth soft and supple on the drying cylinders.

Such padding liquors are represented by the following formulæ:—

(I.)	115	c.c	caustic soda 70° Tw.
	200	,,	glucose solution 22° Tw.
	50	,,	glycerine.
	635	,,	water.
	1000		

(II.)	115	c.c.	caustic soda 70° Tw.
	75	,,	methylated spirit.
	810	,,	water.
	1000		

Pad in a 3-bowl mangle and dry very carefully on a cylinder drying machine arranged as described below, thus:—

1st	stack of cylinders:	moderately cool.
2nd	,, ,,	warmer.
3rd	,, ,,	just hot enough to complete the drying.

After drying, wash well, sour in dilute sulphuric acid, wash, and dry. Recipes I. and II. may be combined if desired.

A similar method is adopted when saponification is effected by means of potassium carbonate, but in this case the goods are steamed after padding and drying. Thus:—

Pad in a solution of—

(III.)	250	grms.	potassium carbonate.
	50	c.c.	methylated spirit.
	1000	,,	water.

Dry carefully over an ordinary drying machine, steam for 5 minutes in a rapid ager at 102°–104° C. (216°–220° F.), wash, and dry. Souring is not necessary if the goods are intended for dyeing with Direct dyestuffs for discharge styles.

Where padding machines are not available, saponification is best carried out in an elliptical winch dye beck with a solution of soda-ash at the rate of 20 grms. per litre, or in a solution of caustic soda equivalent to 10 per cent. caustic soda on the weight of acetate rayon contained in the goods under treatment. The goods are run in the beck for $\frac{3}{4}$–1 hour at 70°–75° C., and afterwards washed, soured, washed, and dried. Although, with care, this method of saponification, in the rope form, may be carried out, in some cases,

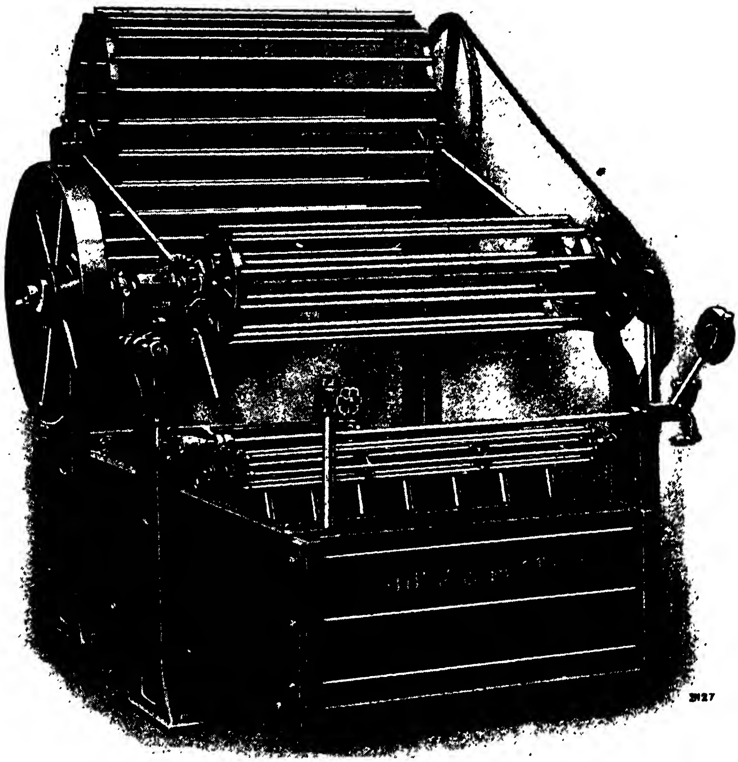


FIG. 89.—Elliptical winch dyeing machine.

in an ordinary dye beck, it must be noted that this type of machine is totally unsuited for dealing with many of the more delicate classes of rayon fabrics. Goods manufactured from rayons, whether mixed with cotton or not, are much more fragile in the wet state than the bulk of materials composed of the natural fibres alone. Those of the finest texture—crêpes, georgettes, ninons, voiles, and others of similar delicate structure—are extremely susceptible to mechanical injury, and require most careful handling in process to preserve them from such defects as fraying, tearing, distortion of threads, rubbing marks, and bruised fibres—defects which are due to friction and excessive tension brought about by irregular running, snatch, or jerkiness between winch and dye beck and entanglements in the latter.

Hence saponification is best conducted in a machine of the type shown in fig. 89. This machine has been specially designed to give a constant speed to the cloth as it passes through the liquor, and to eliminate, as far as

is mechanically possible, all risk of damage arising out of snatch and undue tension on the fabric. Both winches are positively driven, and all undriven parts are mounted in ball bearings so as to ensure a minimum amount of tension on the cloth. The elliptical winch dyeing machine is also provided with an automatic knock-off motion which comes into operation immediately there is any indication of undue tension, stopping the machine before the danger point is reached. In other respects it operates in the same manner as the elliptical winch washing and scouring machine already described and illustrated in fig. 71 (*q.v.*) ; and it may be used for the same purposes.

Partial saponification alters completely the chemical nature and dyeing properties of the outer parts of cellulose acetate fibres, but, if conducted under suitable conditions, it has very little effect on their silky appearance and does nothing to depreciate their commercial value, whilst adding considerably to their technical possibilities. Apart from direct-printed styles, which can be executed in any ordinary steam colours, the fact that saponified acetate rayon can be dyed and discharged by exactly the same dyestuffs and materials as are in current use for cotton and viscose rayon is, of itself, of great technical interest, since the saponification process affords the only means, at present available, of obtaining a full and varied range of really satisfactory discharge effects on cellulose acetate rayon fabrics.

After saponification, acetate rayon goods may, for all practical purposes, be regarded as regenerated cellulose rayon, and be dealt with according to any of the methods described for the printing or dyeing of viscose materials.

Saponification, entailing as it does extra processes of padding, drying, washing, and souring, adds to the cost of production, however, and as a process it can be considered only as a temporary expedient, a convenient means to an end, to be discarded as soon as new types of dyestuffs are introduced which are capable of being dyed, and discharged to a good and permanent white, on pure acetate rayon fabrics.

Solacet Dyestuffs.—Apropos of the desirability of eliminating saponification from acetate rayon dyeing processes, it is interesting to note that, early in the present year (1936), Imperial Chemical Industries, Ltd., introduced the two first members—Solacet fast scarlet B.S. and Solacet fast crimson B.S.—of an entirely new series of water-soluble products which dye pure acetate rayon from a simple saline dyebath. Other members of the series, giving various shades of yellow, orange, red, brown, blue, and violet, have also been prepared and will become available in due course.

Compared with Dispersol and Duranol dyestuffs, the Solacet colours consist of analogous azo and aminoanthraquinone compounds containing special solubilising groups which, unlike ordinary sulphonic groups, do not interfere with the fixation of the colour on the fibre.

These new dyestuffs, in addition to their valuable property of being readily soluble in water, possess also excellent affinity for the unsaponified acetate fibre, are of good all-round fastness and are free from the defect of "marking-off" on steaming—all qualities which fit them admirably for the direct printing of acetate rayon materials upon which, even in pale shades, they yield smooth and level prints. Owing to their solubility (in some instances enhanced by an addition of Solution Salt S.V.), the Solacet colours are particularly useful for the printing of pile fabrics where good and even penetration is highly desirable and where trouble, in this connection, is liable to arise when insoluble dispersed acetate rayon dyestuffs are employed in compound shades.

For similar reasons Solacet fast scarlet B.S., Solacet fast crimson B.S., and other colours of the series are suitable for dyeing all forms of acetate rayon.

Their affinity for the fibre is increased by additions of common or Glauber's salt to the dye bath ; hence they are especially interesting for the dyeing of heavy crêpe and goods of like texture, where good penetration is essential, since the rate of dyeing and exhaustion of the dye bath (which determine largely the degree of penetration) can be controlled by appropriate additions of salt to the dye bath as is done in dyeing Direct colours on cotton. In this respect they are much more amenable than dispersed dyestuffs, which are apt to rush on the fibre at too great a rate, with consequent liability to uneven dyeing.

Solacet dyestuffs may be mixed, if desired, with Duranol and Dispersol dyestuffs for the dyeing of plain compound shades on acetate rayon, the presence of common salt or sodium sulphate in the dye bath having no effect on the Duranol and Dispersol colours. Also, as might be expected from their mode of dyeing and from the fact that they have no affinity for cotton or viscose fibres, the Solacet dyestuffs may be applied in conjunction with C.R. Chlorazol and other Direct dyestuffs for the production of either plain shades or two-colour effects on mixed fabrics of cotton and acetate rayon.

Ground shades dyed on acetate rayon with Solacet fast scarlet B.S. and Solacet fast crimson B.S. are dischargeable to a good white by the Formosul-calcium (or zinc) sulphocyanide process, or by other processes given on page 996, employing Decroline, Hydrosulphite B.Z. or similar zinc sulphoxylates such as Redusol Z., etc.

Dyeing Process.—Solacet dyestuffs are dyed from a bath containing either common salt or Glauber's salt, the dyeing being conducted at a temperature of 80°–85° C. (176°–185° F.) for ¾ hour. For dyeing heavy fabrics a minimum of salt is added at the outset in order to ensure thorough penetration, further additions being made at intervals during the process until the dye bath is more or less exhausted. 1½ per cent. of dyestuff yields a fairly full shade.

Printing Process.—The dyestuffs are simply dissolved in hot water and mixed with the necessary quantity of gum thickening. In some cases an addition of ½–2 per cent. of Solution Salt S.V. is beneficial.

Printing Recipe.

	Red.	Crimson.
Solacet fast scarlet B.S. .	10– 20 grms.	..
,, ,, crimson B.S. .	..	10– 20 grms.
Solution Salt S.V. . .	..	5– 20 ,,
Hot water . . .	400–390 ,,	400–375 ,,
Dissolve and stir into—		
Gum Senegal thickening .	590 ,,	585 ,,
	1000	1000

After printing, steam for ½ hour at 100° C., wash well in water, and dry.

The Solacet dyestuffs are of good fastness to light, washing, alkalies, and steaming (but poor to chlorine), and as they are also applied easily in dyeing and printing, and are dischargeable, they are likely to be accorded ready acceptance by the industry.

APPENDIX.

1. VARIEGATED AND MARBLED EFFECTS ON TEXTILE FABRICS.

A NOVEL process for obtaining, on textile fabrics, colour effects of a variegated and marbled character, without the use of engraved rollers, blocks, or stencils, forms the subject-matter of a patent taken out by E. Schofield and others.[1]

The colours are applied to the *under side* of a horizontally travelling fabric by means of rotating brushes dipping into a colour box beneath, and, to the *upper side*, by allowing them to drop upon the cloth from a series of suitably placed colour cans provided with taps to control the rate of flow.

The brushing and dropping arrangements may be operated either singly or in combination according to the effect desired ; and, in both cases, the consistency of the colour and the quantity of it applied are such as to ensure complete penetration of the fabric, thus producing reversible effects. Before passing over the drying machine, all surplus colour is removed from the cloth by Wimpenny rollers. These rollers are simply smooth brass rollers which, being driven independently at a speed slightly higher than that of the cloth, and in contact with it, pick up the surplus colour and transfer it to the doctors with which they are fitted. From the doctors the colour flows away into any convenient receptacle.

A section of the machine employed for carrying out the process is shown in fig. 90.

(W) is a wince, or cylindrical frame, built up of sixteen transverse bars upon which are secured any number of brushes (B B) in any arrangement desired. (W) is driven by change gearing from the main driving shaft of the machine so that its speed in relation to that of the cloth (C C C) may be varied as required to produce certain effects. The cloth (C C C) enters the machine over tension and scrimp rails and under the adjustable roller (E) which serves to regulate its pressure on the rotating brushes (B B). Colour is supplied to the brushes from the colour box (F), into which they dip as they revolve. The colour cans (D) are hung on a bar or rail extending across the machine, and are supplied from colour-storage tanks (S) above. As the cloth passes through the machine it first receives a charge of colour, on its under side, from the brushes, and then (if desired) a second charge, on its upper side, from the taps (T) of the colour cans (D), the taps being regulated to drip at predetermined intervals. Before entering the drying machine, excess of colour is removed from the surface of the cloth by the Wimpenny rollers (G G), and from these in turn by the doctors (X X). The whole mechanism is mounted in a strong frame (A A A) and is actuated in any suitable manner. After drying over steam-heated cylinders the cloth follows the usual course appropriate to the class of colours or discharges with which it has been treated.

As it is tedious to turn off, and regulate afresh, the taps (T) when the

[1] English patent No. 139373, 1920 (The Calico Printers' Association, Ltd., E. Schofield and F. Farnworth).

machine is temporarily stopped, catching troughs (not shown in fig. 90) are arranged to slide under the taps and catch the colours, which are subsequently returned to the storage tank (S).

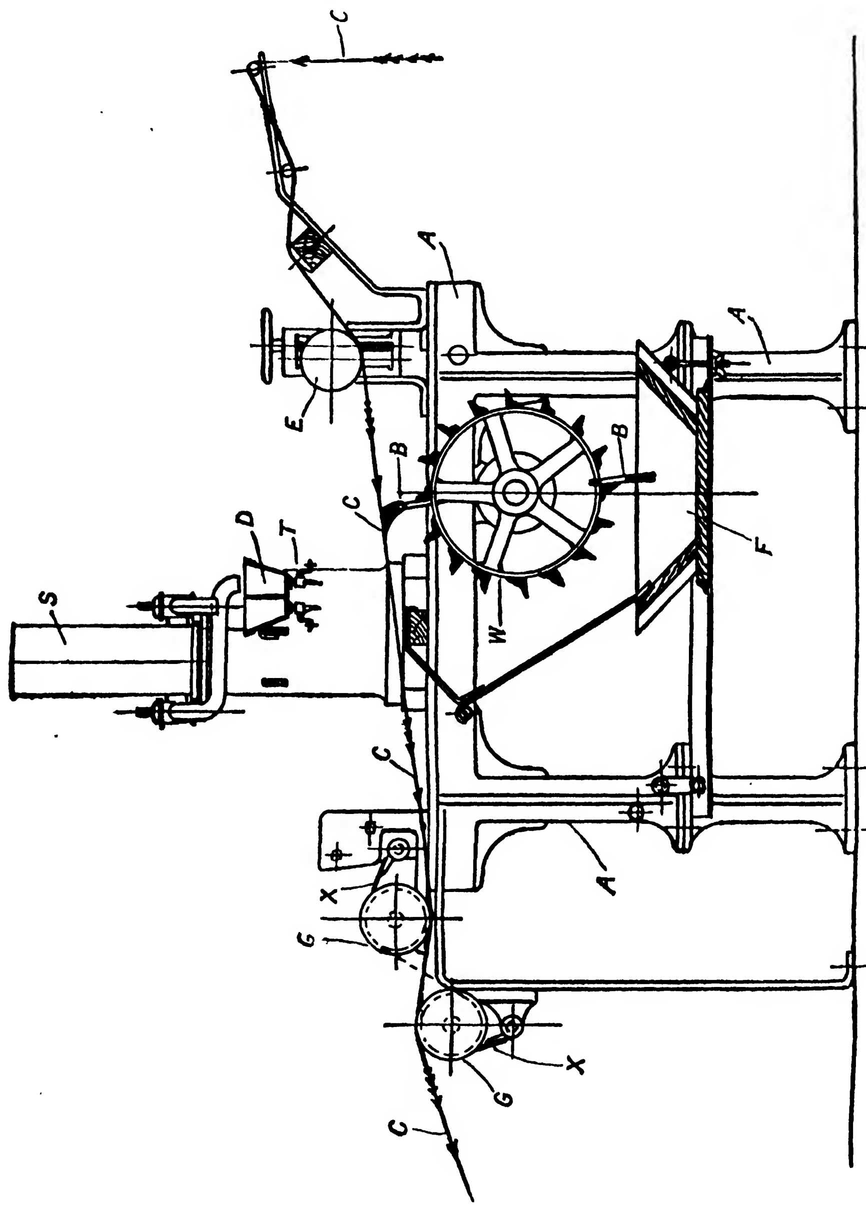


Fig. 90.—Brush and Drop Machine.

For certain styles of work the colour cans (D) may be arranged to traverse, or move to and fro, across and above the travelling fabric, and a similar motion may be imparted to the Wimpenny rollers. A good deal of variety can also be obtained by varying the speeds of the brushes and cloth respectively, and also by the degree of pressure exerted by the cloth on the brushes.

By altering the positions, number, and sizes of the brushes attached to the bars of the wince, and by using a divided colour box, it is obvious that a great diversity of stripes and transverse undulating and zigzag bands, in several colours, can be obtained readily by this machine. Similarly by dropping different colours on the upper side of the cloth and by giving the colour cans a traversing motion it is possible to obtain an almost equal variety of marbled effects. Both these types of decoration can be reproduced for repeat orders.

The process is applicable to many classes of work; but its characteristic features are best displayed, perhaps, in those composite Indigo styles produced for the African market. One of the simplest of these is executed by printing Indigo-dyed cloth with Azoic colours (Red or Claret) and a lead yellow, and then, after washing and drying, discharging certain portions of the blue ground by brushing on a chlorate discharge. The results obtained are very striking. Where the brushes have first come into contact with the cloth the Indigo ground is completely discharged, leaving a pure red, yellow, and white pattern; then, as the brushes gradually work out of touch with the cloth, the discharge becomes weaker and weaker, and, in some cases, disappears altogether, until the next row of brushes comes into action. The final effect is of a red, yellow, and white pattern gradually emerging from a background of blue, brown, and green. Corresponding, but different, effects are obtained if the discharge is dropped on the cloth as already described.

Almost any kind of colour, resist or discharge, whether chemical or mechanical (wax, resin, etc.), may be used, so that the process lends itself to a wide range of styles.

2. PROCESS FOR PREVENTING THE TENDERING OF GOODS DYED WITH SULPHUR COLOURS.

It has long been known to dyers and calico printers that goods dyed with Sulphur colours are liable, sooner or later, to lose considerably in tensile strength. This may occur during any of the various processes immediately following the dyeing operation, or it may not take place until the goods have been stored many months. Sometimes no "tendering" at all takes place; while, on the other hand, cases are frequently cited where goods have left the works in perfect condition, and have been found to have become quite tender on arrival at their destination in some far eastern port.

The cause of tendering has been fully investigated by J. E. Pilling,[1] who came to the conclusion that it was due entirely to the presence of sulphuric acid; and, further, that this sulphuric acid was formed not necessarily by the oxidation of sodium sulphide, or polysulphides (often present in the dyestuff), but by the oxidation of the colour-molecule itself, or by the oxidation of sulphurous acid to which mixed goods are subjected in the stoving (sulphuring) process, and which is always present in the atmosphere of manufacturing districts.

Most of the methods recommended for overcoming the tendering action of Sulphur dyestuffs depend either upon the use of oxidising agents (to further the oxidation of the dyestuff during process), or upon an after-treatment with salts capable of neutralising free mineral acids.

In this latter connection the following compounds have been recommended: soap, sulphite of soda, carbonate of soda, and the formates and acetates of lime

[1] *Journal of Society of Dyers and Colourists*, Feb. 1906.

and soda. Up to a certain point these salts are undoubtedly efficient, but they possess the disadvantage of being soluble, and, consequently, when the goods are washed they are removed from the fibre and become inoperative.

The employment of bichromates and acetic acid with the idea of completing the oxidation of the colouring matter at once has not been found to attain its object with any degree of certainty.

In the process of G. E. Holden [1] the drawbacks connected with the application of soluble neutralising salts are obviated by the fixation on the fibre of an insoluble calcium salt which reacts quantitatively with the sulphuric acid as it is produced, and in that way provides a permanent and effective method of preventing the tendering of the dyed goods.

The process, which is very simple, consists in treating the dyed goods in a 1 per cent. solution of tannic acid at 40° C., squeezing, passing through lime water, and finally washing.

Goods dyed with a number of representative Sulphur blacks, blues, browns, etc., when treated in this way and exposed, along with untreated samples, to a temperature of 120° C. for twenty hours, retained their original strength unimpaired, whilst the untreated samples all became tender, and many of them quite rotten.

In addition to preventing a loss in tensile strength, this process has other advantages, namely: (*a*) in some cases it *increases* the tensile strength of the fibres; (*b*) in the case of blacks especially it improves the depth and tone so as sometimes to allow of 10 per cent. less dyestuff being used to produce a given shade; (*c*) it adds to the weight of the goods; and (*d*) it is said to increase the power of the goods to absorb starches (in finishing).

Equally good results are obtained by replacing lime water by any other suitable salt of calcium, barium, or strontium; and soda ash may be used in place of tannic acid, although the tannates have been found to yield by far the best results.

[1] *Journal of Society of Dyers and Colourists*, April 1910.

3. LIST OF THE MORE IMPORTANT AUXILIARY PRODUCTS USED IN TEXTILE PRINTING AND DYEING.

Trade Name.	Description.	Use.
Acetin N.	Mixture of mono-, di-, and tri-acetyl glycerine.	Solvent for Basic and Chrome colours.
Acid F.	β-Naphtholsulphonic acid F.	Shading of Paranitraniline reds.
Aktivin	Sodium toluene-*p*-sulphonchloroamide	Scouring of rayon and cotton goods.
Algosol	Sodium benzylsulphanilate	Solvent for Vat colours.
Anon	Cyclohexanone	,, ,, cellulose esters, Sericose, etc.
Astol A.	Trichlorethylene emulsion	Scouring of woollen and rayon goods: removal of oil stains.
Azoguard	Naphthalene trisulphonic acid	Stabilising of diazo compounds.
Azotol C.	Chrysoïdine R.	Printing of Azoic colours.
Britulite	Sodium sulphoxylate-formaldehyde	,, ,, Vat colours and Discharges on Azoic and Direct colours.
Brown salt G.	Vesuvine	Browns coupled with diazo-*p*-nitraniline.
,, ,, R.	Chrysoïdine	Browns coupled with diazo-*p*-nitraniline.
Calgon	Sodium metaphosphate	Dispersing agent.
Cirrasol S.A.	Emulsion based on the higher alcohols	Anti-electrostatic softening agent for acetate rayon finishes, etc.
Decalin	Decahydronaphthalene	Penetrating and dispersing agent.
Decrolin	Basic zinc sulphoxylate-formaldehyde	Stripping agent.
,, soluble conc.	Normal ,, ,, ,,	Stripping agent and discharge printing.
,, A.Z.A.	Basic zinc sulphoxylate-acetaldehyde	Stripping agent.
Dehapan O.	Preparation of urea and cresylic acid.	Solvent for Indigosols, Vat and Chrome colours.
Dekol	Wood bisulphite liquor	Dyeing assistant.
Developer A.	β-Naphthol	Developer for diazotised Direct colours.
,, A.D.	Aminodiphenylamine	Developer for diazotised Direct colours.
,, A.N.	Aminonaphtholsulphonic acid	Developer for diazotised Direct colours.
,, B.	Ethyl-β-naphthylamine	Developer for diazotised Direct colours.
,, C.	*m*-Phenylenediamine	Developer for diazotised Direct colours.
,, E.S.	2 : 3-Dioxynaphthalenesulphonic acid	Developer for diazotised Direct colours.
,, F.	Resorcin	Developer for Direct, Ionamine, and Cellitazol colours.
,, G.	An aminonaphtholsulphonic acid.	Developer for Direct colours.
,, H.	*m*-Toluylenediamine	,, ,, ,,
,, J.	Phenol	,, ,, ,,
,, N.B.	Nitrobenzidine	,, ,, ,,
,, O.N.	β-Oxynaphthoic acid	Developer for Ionamine and Cellitazol colours.
,, Z.	Phenylmethylpyrazolone	Developer for Direct colours.
,, for red	β-Naphthol	,, ,, ,,
,, maroon	α-Naphthol	,, ,, ,,
,, yellow	Phenol	,, ,, ,,
Diastasan	Malt preparation	De-sizing for bleaching, etc.
Diastophor	,, ,,	,, ,, ,, ,,

Trade Name.	Description.	Use.
Diethylene glycol .	Dihydroxydiethyl ether	Printing of Indigosol, Vat, Basic, and Acid colours.
Diphenyl black base M.	*p*-Aminodiphenylamine	Printing of oxidation blacks.
Diphenyl black oil D.O.	,, ,, dissolved in aniline	,, ,, ,, ,,
Discharge salt W. .	Calcium salt of Leucotrope disulphonic acid.	Discharging of Indigo and Vat colours.
Ethylene glycol .	Ethylene alcohol or dihydroxyethane	Printing of Indigosol, Soledon, Vat, etc., colours.
Fast Colour Bases .	See text under *Naphthol A.S.* . .	Printing of Azoic colours.
,, ,, Salts .	,, ,, ,, ,,	,, ,, ,, ,,
Fermasol . .	Pancreatic gland extract . . .	Ferment for de-sizing.
Fibrit D. . .	Diethylene glycol	Solvent for Basic, Acid, Indigosol, and Vat colours.
Fixanol . .	Salt of a quaternary ammonium base .	Fixation of Direct dyestuffs.
Formosul . .	Sodium sulphoxylate-formaldehyde .	Discharging of Azoic, Vat, and Direct dyes.
,, C.L. .	Formosul + Metabol F. (*q.v.*) . . .	Discharging of Azoic, Vat, and Direct dyes.
,, C.W. .	Formosul + zinc oxide	Discharge printing on wool and silk.
Fuscamine G. .	*m*-Aminophenol	Oxidation browns.
Gardinols . .	Sulphates of higher fatty alcohols . .	Detergents and wetting-out agents.
Glycecine A. . .	Thiodiglycol (*q.v.*)	Solvent for Indigosol, Vat, and some Azoic colours.
Hexalin . .	Cyclohexanol	Penetrating agent.
Hydros . . .	Sodium hydrosulphite ($Na_2S_2O_4$) . .	Printing and dyeing of Vat colours.
Hyraldite C. extra .	Sodium sulphoxylate-formaldehyde .	Printing of Vat colours and various discharge styles.
,, C.L. .	Hyraldite C. extra + Leucotrope W. .	Discharging of Indigo, Vat, and Azoic colours.
,, C.W. extra	,, ,, ,, + zinc oxide . .	Discharging of Acid colours, etc., dyed on woollen goods.
Igepon A. . . .	Long-chain fatty acid ester of type $CH_3(CH_2)_nCOOC_2H_4.SO_3Na$.	Dispersing and deterging agent.
,, T. . .	Long-chain fatty acid amide of type $CH_3(CH_2)_nCO.NH.C_2H_4.SO_3Na$.	,, ,, ,, ,,
Indigosol developer D.	Diethyl tartrate	Indigosol and Soledon printing.
Indigosol developer G.A.	Ethylene glycol	,, ,, ,, ,,
Irgasol . . .	Ethylene glycol monoethyl ether . .	Solvent for Basic, Acid, Chrome, and other dyestuffs.
Leucophenine O. .	See Leucotrope O.	See Leucotrope O.
,, W. .	,, ,, W.	,, ,, ,,
Leucotrope O. .	Dimethylphenylbenzylammonium chloride.	Discharging and resisting of Indigo and Vat colours.
,, W. .	Calcium salt of disulphonated Leucotrope O.	Discharging and resisting of Indigo and Vat colours.
Lissapol A. / ,, C. .	Sulphonated long-chain fatty alcohols of general type $CH_3(CH_2)_nOSO_3Na$.	Dispersing, deterging, and softening agents.
Lizarol D. . .	Formaldehyde compound of ricinoleic acid.	Printing of Alizarin reds on unoiled cloth.
Ludigol . .	Sodium *m*-nitrobenzenesulphonate .	Reserves under Vat colours and reduction discharges.

Trade Name.	Description.	Use.
Mercerol . .	o-Cresol + cyclohexanol	Mercerising assistant.
Metabol F. . .	Leucotrope W. (*q.v.*)	Indigo and Vat colour discharges.
Metachrome mordant.	Mixture of potassium bichromate (1 part) and ammonium sulphate ($2\frac{1}{2}$ parts).	Dyeing of wool with Metachrome and certain Direct dyestuffs.
Methyl Anon . .	Methylcyclohexanone	Solvent for cellulose esters, Sericose, etc.
Methyl Hexalin .	Methylcyclohexanol	Penetrating and dispersing agent.
Monacide . .	β-Naphtholsulphonic acid F. . .	Shading of Paranitraniline reds.
Monopol Brilliant Oil.	Ammonium salt of highly sulphonated castor oil.	Preparing for, and printing of, Azoic colours.
Naphthol A.S. (group).	See text under *Naphthol A.S.*	
Nekal A. . .	Sodium isopropylnaphthalenesulphonate	Wetting-out and penetrating agent.
,, B.X. . .	Pure form of Nekal A.	,, ,, ,, ,,
Nitrazol C. . .	Stable salt of diazo-p-nitraniline . .	Dyeing of Azoic colours and developing of Direct dyeings.
Nitrosamine red .	Sodium salt of p-nitrobenzene anti-diazohydroxide.	Printing of Paranitraniline red.
Nitroso base M. .	Nitrosodimethylaniline	,, ,, Nitroso blues.
Novofermasol .	Pancreatic gland preparation . .	De-sizing agent.
Ortamine . .	o-Anisidine	Oxidation browns.
Paradurol . .	Naphthalenetrisulphonic acid . .	Stabilisation of diazo-paranitraniline.
Paramine . .	p-Phenylenediamine	Oxidation browns.
Para soap . .	Ammonium ricinoleate	Naphthol prepares.
Perminal K.B. .	Pine oil emulsion	Kier boiling, fat solvent, wetting-out, and dispersing agent.
,, merc. .	See Mercerol	Mercerising assistant.
,, W. . .	Alkylated mineral oil sulphonate . .	Kier boiling and vat dyeing as emulsifying and penetrating agent.
Phenamine . .	m-Aminophenol	Oxidation browns.
Rapidase . .	Diastasic preparation	De-sizing agent.
Rapidazol dyestuffs	See text under *Naphthol A.S.* . .	Printing of Azoic colours.
Rapid Fast ,,	,, ,, ,, ,,	,, ,, ,, ,,
Rapidogen ,,	,, ,, ,, ,,	,, ,, ,, ,,
Red-oil . . .	See Lizarol D.	,, ,, Alizarin reds.
Redusol Z. . .	Zinc sulphoxylate-formaldehyde . .	Discharge printing: Stripping agent.
Repellats . .	Salts of dodecylpyridinium laurate type .	Softening and dispersing agents.
Reservol B. . .	Manganese m-nitrobenzenesulphonate .	Resist under Vat colours and Rongalite discharges.
Rongalite C. . .	Sodium sulphoxylate-formaldehyde .	Direct and discharge printing of Vat, Azoic, and Direct colours.
,, C.L. .	Sodium sulphoxylate-formaldehyde + Leucotrope W.	Discharging of Vat, Azoic, and Direct colours.
,, C.W. .	Sodium sulphoxylate-formaldehyde + zinc oxide.	Discharge printing on wool and silk.
Sapamin . .	Quaternary ammonium salt of oleic acid	Deterging agent.
Sextol . . .	Cyclohexanol	Penetrating agent.
Sextone . .	Cyclohexanone	,, ,, and solvent for cellulose esters.
Shading salt . .	β-Naphtholsulphonic acid F. . .	Shading of Paranitraniline reds.
Shirlan . . .	Salicylanilide	Fungicide: Mildew preventive.
,, N.A. . .	Water-soluble form of Shirlan . .	Fungicide: Mildew preventive in finishing.
Solidogen . .	Compound of p-formaldehyde and o-toluidine.	Developer for Direct colours.

Trade Name.	Description.	Use.
Solution Salt S.V. .	Sodium dibenzylsulphanilate . .	Solvent for Indigosol, Soledon, leuco-Vat colours, etc.
„ „ B. .	„ monobenzylsulphanilate . .	Solvent for Indigosol, Soledon, leuco-Vat colours, etc.
Solvenol . .	„ „	Solvent for Indigosol, Soledon, leuco-Vat colours, etc.
Spencol . .	See Lizarol D.	Printing of Alizarin red.
Tetracarnit . .	Pyridine bases	Wetting-out and penetrating agent.
Tetralin . .	Tetrahydronaphthalene	Solvent and penetrating agent.
Thiodiglycol . .	Dihydroxydiethyl sulphide (Glyecine A.)	Solvent for Indigosols, Vat, Basic, and Acid colours.
Triethanolamine .	Trihydroxytriethylamine	Printing of Vat, Sulphur, Acid, and certain Dispersed colours on rayon, etc.
Waxol P. . .	Paraffin wax emulsion	Softening and waterproofing agent.
„ T. . .	Tallow emulsion	Softening agent in finishes.
„ W. . .	Paraffin wax and aluminium acetate emulsion.	Waterproofing of gaberdines, etc.
Westoran (and Westropol).	Soap and trichlorethylene	Scouring agent.
Westron . .	Tetrachlorethane	„ „ and fat solvent.
Westrosol . .	Trichorethylene	„ „ „ „
Zinc Formosul .	Basic zinc sulphoxylate-formaldehyde .	Stripping agent.

4. COMPARATIVE TABLE OF SPECIFIC GRAVITIES AND HYDROMETER DEGREES, BAUMÉ AND TWADDLE.

Specific Gravity at 59° F.	Degrees Baumé.	Degrees Twaddle.	Specific Gravity at 59° F.	Degrees Baumé.	Degrees Twaddle.	Specific Gravity at 59° F.	Degrees Baumé.	Degrees Twaddle.
1·000	0	0	1·290	32·4	58	1·580	53·0	116
1·005	0·7	1	1·295	32·8	59	1·585	53·3	117
1·010	1·4	2	1·300	33·3	60	1·590	53·6	118
1·015	2·1	3	1·305	33·7	61	1·595	53·9	119
1·020	2·7	4	1·310	34·2	62	1·600	54·1	120
1·025	3·4	5	1·315	34·6	63	1·605	54·4	121
1·030	4·1	6	1·320	35·0	64	1·610	54·7	122
1·035	4·7	7	1·325	35·4	65	1·615	55·0	123
1·040	5·4	8	1·330	35·8	66	1·620	55·2	124
1·045	6·0	9	1·335	36·2	67	1·625	55·5	125
1·050	6·7	10	1·340	36·6	68	1·630	55·8	126
1·055	7·4	11	1·345	37·0	69	1·635	56·0	127
1·060	8·0	12	1·350	37·4	70	1·640	56·3	128
1·065	8·7	13	1·355	37·8	71	1·645	56·6	129
1·070	9·4	14	1·360	38·2	72	1·650	56·9	130
1·075	10·0	15	1·365	38·6	73	1·655	57·1	131
1·080	10·6	16	1·370	39·0	74	1·660	57·4	132
1·085	11·2	17	1·375	39·4	75	1·665	57·7	133
1·090	11·9	18	1·380	39·8	76	1·670	57·9	134
1·095	12·4	19	1·385	40·1	77	1·675	58·2	135
1·100	13·0	20	1·390	40·5	78	1·680	58·4	136
1·105	13·6	21	1·395	40·8	79	1·685	58·7	137
1·110	14·2	22	1·400	41·2	80	1·690	58·9	138
1·115	14·9	23	1·405	41·6	81	1·695	59·2	139
1·120	15·4	24	1·410	42·0	82	1·700	59·5	140
1·125	16·0	25	1·415	42·3	83	1·705	59·7	141
1·130	16·5	26	1·420	42·7	84	1·710	60·0	142
1·135	17·1	27	1·425	43·1	85	1·715	60·2	143
1·140	17·7	28	1·430	43·4	86	1·720	60·4	144
1·145	18·3	29	1·435	43·8	87	1·725	60·6	145
1·150	18·8	30	1·440	44·1	88	1·730	60·9	146
1·155	19·3	31	1·445	44·4	89	1·735	61·1	147
1·160	19·8	32	1·450	44·8	90	1·740	61·4	148
1·165	20·3	33	1·455	45·1	91	1·745	61·6	149
1·170	20·9	34	1·460	45·4	92	1·750	61·8	150
1·175	21·4	35	1·465	45·8	93	1·755	62·1	151
1·180	22·0	36	1·470	46·1	94	1·760	62·3	152
1·185	22·5	37	1·475	46·4	95	1·765	62·5	153
1·190	23·0	38	1·480	46·8	96	1·770	62·8	154
1·195	23·5	39	1·485	47·1	97	1·775	63·0	155
1·200	24·0	40	1·490	47·4	98	1·780	63·2	156
1·205	24·5	41	1·495	47·8	99	1·785	63·5	157
1·210	25·0	42	1·500	48·1	100	1·790	63·7	158
1·215	25·5	43	1·505	48·4	101	1·795	64·0	159
1·220	26·0	44	1·510	48·7	102	1·800	64·2	160
1·225	26·4	45	1·515	49·0	103	1·805	64·4	161
1·230	26·9	46	1·520	49·4	104	1·810	64·6	162
1·235	27·4	47	1·525	49·7	105	1·815	64·8	163
1·240	27·9	48	1·530	50·0	106	1·820	65·0	164
1·245	28·4	49	1·535	50·3	107	1·825	65·2	165
1·250	28·8	50	1·540	50·6	108	1·830	65·5	166
1·255	29·3	51	1·545	50·9	109	1·835	65·7	167
1·260	29·7	52	1·550	51·2	110	1·840	65·9	168
1·265	30·2	53	1·555	51·5	111	1·845	66·1	169
1·270	30·6	54	1·560	51·8	112	1·850	66·3	170
1·275	31·1	55	1·565	52·1	113	1·855	66·5	171
1·280	31·5	56	1·570	52·4	114	1·860	66·7	172
1·285	32·0	57	1·575	52·7	115	1·865	67·0	173

Note.—The degrees in Twaddle's hydrometer bear a direct relationship to the specific gravity and may be obtained from the same by the following formula in which d represents the specific gravity and n the number of degrees Twaddle: $n = \frac{1000d - 1000}{5}$. On the other hand, by the formula $d = \frac{5n + 1000}{1000}$ the degrees Twaddle are converted into the corresponding specific gravity. For values below sp.g. 2·0, the degrees Twaddle may also be obtained from the specific gravity by moving the decimal point two figures to the right, striking off the first figure and multiplying the rest by 2, as per the following example:—

Specific gravity 1·133:
113·3:
13·3 × 2:
26·6° Twaddle.

Comparison of Hydrometer Degrees Baumé with the Specific Gravity of Liquids lighter than Water.

Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.	Degrees Baumé.	Specific Gravity.
11	0·993	16	0·960	21	0·930	26	0·901
12	0·987	17	0·954	22	0·924	27	0·896
13	0·980	18	0·948	23	0·918	28	0·890
14	0·973	19	0·942	24	0·913	29	0·885
15	0·967	20	0·936	25	0·907	30	0·880

A special Baumé hydrometer is used for liquids lighter than water.

5. COMPARISON OF THERMOMETRIC SCALES.

Centigrade.	Réaumur.	Fahrenheit.	Centigrade.	Réaumur.	Fahrenheit.	Centigrade.	Réaumur.	Fahrenheit.
+100	+80	+212	+53	+42·4	+127·4	+ 6	+ 4·8	+42·8
99	79·2	210·2	52	41·6	125·6	5	4	42
98	78·4	208·4	51	40·8	123·8	4	3·2	39·2
97	77·6	206·6	50	40	122	3	2·4	37·4
96	76·8	204·8	49	39·2	120·2	2	1·6	35·6
95	76	203	48	38·4	118·4	1	0·8	33·8
94	75·2	201·2	47	37·6	116·6	0	0	32
93	74·4	199·4	46	36·8	114·8	− 1	− 0·8	30·2
92	73·6	197·6	45	36	113	2	1·6	28·4
91	72·8	195·8	44	35·2	111·2	3	2·4	26·6
90	72	194	43	34·4	109·4	4	3·2	24·8
89	71·2	192·2	42	33·6	107·6	5	4	23
88	70·4	190·4	41	32·8	105·8	6	4·8	21·2
87	69·6	188·6	40	32	104	7	5·6	19·4
86	68·8	186·8	39	31·2	102·2	8	6·4	17·6
85	68	185	38	30·4	100·4	9	7·2	15·8
84	67·2	183·2	37	29·6	98·6	10	8	14
83	66·4	181·4	36	28·8	96·8	11	8·8	12·2
82	65·6	179·6	35	28	95	12	9·6	10·4
81	64·8	177·8	34	27·2	93·2	13	10·4	8·6
80	64	176	33	26·4	91·4	14	11·2	6·8
79	63·2	174·2	32	25·6	89·6	15	12	5
78	62·4	172·4	31	24·8	87·8	16	12·8	3·2
77	61·6	170·6	30	24	86	17	13·6	1·4
76	60·8	168·8	29	23·2	84·2	18	14·4	− 0·4
75	60	167	28	22·4	82·4	19	15·2	2·2
74	59·2	165·2	27	21·6	80·6	20	16	4
73	58·4	163·4	26	20·8	78·8	21	16·8	5·8
72	57·6	161·6	25	20	77	22	17·6	7·6
71	56·8	159·8	24	19·2	75·2	23	18·4	9·4
70	56	158	23	18·4	73·4	24	19·2	11·2
69	55·2	156·2	22	17·6	71·6	25	20	13
68	54·4	154·4	21	16·8	69·8	26	20·8	14·8
67	53·6	152·6	20	16	68	27	21·6	16·6
66	52·8	150·8	19	15·2	66·2	28	22·4	18·4
65	52	149	18	14·4	64·4	29	23·2	20·2
64	51·2	147·2	17	13·6	62·6	30	24	22
63	50·4	145·4	16	12·8	60·8	31	24·8	23·8
62	49·6	143·6	15	12	59	32	25·6	25·6
61	48·8	141·8	14	11·2	57·2	33	26·4	27·4
60	48	140	13	10·4	55·4	34	27·2	29·2
59	47·2	138·2	12	9·6	53·6	35	28	31
58	46·4	136·4	11	8·8	51·8	36	28·8	32·8
57	45·6	134·6	10	8	50	37	29·6	34·6
56	44·8	132·8	9	7·2	48·2	38	30·4	36·4
55	44	131	8	6·4	46·4	39	31·2	38·2
54	43·2	129·2	7	5·6	44·6	40	32	40

To convert the degrees in one scale into those of another, the following formulæ are used :—

°C to °R multiply by 4, divide by 5.
°C „ °F „ „ 9, „ „ 5, add 32.
°R „ °C „ „ 5, „ „ 4.
°R to °F multiply by 9, divide by 4, add 32.
°F „ °R subtract 32, multiply by 4, divide by 9
°F „ °C „ 32, „ „ 5, „ „ 9

6. SPECIFIC GRAVITY OF SULPHURIC ACID AT 59° F.

(Lunge and Isler.)

Degrees Twaddle.	Per Cent. Sulphuric Acid.	Degrees Twaddle.	Per Cent. Sulphuric Acid.	Degrees Twaddle.	Per Cent. Sulphuric Acid.
2	1·57	62	40·35	122	69·43
4	3·03	64	41·50	124	70·32
6	4·49	66	42·66	126	71·16
8	5·96	68	43·74	128	71·99
10	7·37	70	44·82	130	72·82
12	8·77	72	45·88	132	73·64
14	10·19	74	46·94	134	74·51
16	10·90	76	48·00	136	75·42
18	12·99	78	49·06	138	76·30
20	14·35	80	50·11	140	77·17
22	15·71	82	51·15	142	78·04
24	17·01	84	52·15	144	78·92
26	18·31	86	53·11	146	79·80
28	19·61	88	54·07	148	80·68
30	20·91	90	55·03	150	81·56
32	22·19	92	55·97	152	82·44
34	23·47	94	56·90	154	83·32
36	24·76	96	57·83	156	84·50
38	26·04	98	58·74	158	85·70
40	27·32	100	59·70	160	86·90
42	28·58	102	60·65	162	88·30
44	29·84	104	61·59	164	90·05
46	31·11	106	62·53	165	91·00
48	32·28	108	63·43	166	92·10
50	33·43	110	64·26	167	93·43
52	34·57	112	65·08	168	95·60
54	35·71	114	65·90	168·3*	97·70
56	36·87	116	66·71	168·1*	98·70
58	38·03	118	67·59	168*	99·20
60	39·19	120	68·51	167·7*	99·95

* Sulphuric acid of 97·70 per cent. has the highest specific gravity, whilst that of stronger acid is a little lower.

7. SPECIFIC GRAVITY OF HYDROCHLORIC ACID.

(Lunge and Marchlewski.)

Specific Gravity at 60° F.	Degrees Baumé.	Degrees Twaddle.	100 lbs. contain		1 Gallon contains	
			HCl.	Acid of 32° Tw.	HCl.	Acid of 32° Tw.
			lbs.	lbs.	lbs.	lbs.
1·000	0·0	0·0	0·16	0·49	0·016	0·049
1·005	0·7	1	1·15	3·58	0·12	0·36
1·010	1·4	2	2·14	6·66	0·22	0·67
1·015	2·1	3	3·12	9·71	0·32	0·99
1·020	2·7	4	4·13	12·86	0·42	1·31
1·025	3·4	5	5·15	16·04	0·53	1·64
1·030	4·1	6	6·15	19·16	0·64	1·97
1·035	4·7	7	7·15	22·27	0·74	2·31
1·040	5·4	8	8·16	25·42	0·85	2·64
1·045	6·0	9	9·16	28·53	0·96	2·98
1·050	6·7	10	10·17	31·68	1·07	3·33
1·055	7·4	11	11·18	34·82	1·18	3·67
1·060	8·0	12	12·19	37·97	1·29	4·03
1·065	8·7	13	13·19	41·09	1·41	4·38
1·070	9·4	14	14·17	44·14	1·52	4·72
1·075	10·0	15	15·16	47·22	1·63	5·08
1·080	10·6	16	16·15	50·31	1·74	5·43
1·085	11·2	17	17·13	53·36	1·86	5·79
1·090	11·9	18	18·11	56·41	1·97	6·15
1·095	12·4	19	19·06	59·37	2·09	6·50
1·100	13·0	20	20·01	62·33	2·20	6·86
1·105	13·6	21	20·97	65·32	2·32	7·22
1·110	14·2	22	21·92	68·28	2·43	7·58
1·115	14·9	23	22·86	71·21	2·55	7·94
1·120	15·4	24	23·82	74·20	2·67	8·31
1·125	16·0	25	24·78	77·19	2·78	8·68
1·130	16·5	26	25·75	80·21	2·91	9·06
1·135	17·1	27	26·70	83·18	3·03	9·44
1·140	17·7	28	27·66	86·17	3·15	9·82
1·1425	18·0	..	28·14	87·66	3·22	10·02
1·145	18·3	29	28·61	89·13	3·28	10·21
1·150	18·8	30	29·57	92·11	3·40	10·59
1·152	19·0	..	29·95	93·30	3·45	10·75
1·155	19·3	31	30·55	95·17	3·53	10·99
1·160	19·8	32	31·52	98·19	3·66	11·39
1·163	20·0	..	32·10	100·00	3·73	11·63
1·165	20·3	33	32·49	101·21	3·79	11·79
1·170	20·9	34	33·46	104·24	3·92	12·20
1·171	21·0	..	33·65	104·82	3·94	12·27
1·175	21·4	35	34·42	107·22	4·04	12·60
1·180	22·0	36	35·39	110·24	4·18	13·01
1·185	22·5	37	36·31	113·11	4·30	13·40
1·190	23·0	38	37·23	115·98	4·43	13·80
1·195	23·5	39	38·16	118·87	4·56	14·21
1·200	24·0	40	39·11	121·84	4·69	14·62

8. TABLE OF THE PERCENTAGE OF AQUEOUS NITRIC ACID AT 15° C. (according to Kolb).

Degrees Baumé.	Specific Gravity.	Per Cent. NO_3H.	Degrees Baumé.	Specific Gravity.	Per Cent. NO_3H.
0	1·000	0·2	26	1·220	35·5
1	1·007	1·5	27	1·231	37·0
2	1·014	2·6	28	1·242	38·6
3	1·022	4·0	29	1·252	40·2
4	1·029	5·1	30	1·261	41·5
5	1·036	6·3	31	1·275	43·5
6	1·044	7·6	32	1·286	45·0
7	1·052	9·0	33	1·298	47·1
8	1·060	10·2	34	1·309	48·6
9	1·067	11·4	35	1·321	50·7
10	1·075	12·7	36	1·334	52·9
11	1·083	14·0	37	1·346	55·0
12	1·091	15·3	38	1·359	57·3
13	1·100	16·8	39	1·372	59·6
14	1·108	18·0	40	1·384	61·7
15	1·116	19·4	41	1·398	64·5
16	1·125	20·8	42	1·412	67·5
17	1·134	22·2	43	1·426	70·6
18	1·143	23·6	44	1·440	74·4
19	1·152	24·9	45	1·454	78·4
20	1·162	26·3	46	1·470	83·0
21	1·171	27·8	47	1·485	87·1
22	1·180	29·2	48	1·501	92·6
23	1·190	30·7	49	1·516	96·0
24	1·200	32·1	49·5	1·524	98·0
25	1·210	33·8	49·9	1·530	100·0

9. SPECIFIC GRAVITY OF ACETIC ACID AT 60° F. (Oudemanns).

Specific Gravity.	Percentage of $C_2H_4O_2$.	Specific Gravity.	Percentage of $C_2H_4O_2$.	Specific Gravity.	Percentage of $C_2H_4O_2$.	Specific Gravity.	Percentage of $C_2H_4O_2$.
0·9992	0	1·0363	26	1·0631	52	1·0748	78
1·0007	1	1·0375	27	1·0638	53	1·0748	79
1·0022	2	1·0388	28	1·0646	54	1·0748	80
1·0037	3	1·0400	29	1·0653	55	1·0747	81
1·0052	4	1·0412	30	1·0660	56	1·0746	82
1·0067	5	1·0424	31	1·0666	57	1·0744	83
1·0083	6	1·0436	32	1·0673	58	1·0742	84
1·0098	7	1·0447	33	1·0679	59	1·0739	85
1·0113	8	1·0459	34	1·0685	60	1·0736	86
1·0127	9	1·0470	35	1·0691	61	1·0731	87
1·0142	10	1·0481	36	1·0697	62	1·0726	88
1·0157	11	1·0492	37	1·0702	63	1·0720	89
1·0171	12	1·0502	38	1·0707	64	1·0713	90
1·0185	13	1·0513	39	1·0712	65	1·0705	91
1·0200	14	1·0523	40	1·0717	66	1·0696	92
1·0214	15	1·0533	41	1·0721	67	1·0686	93
1·0228	16	1·0543	42	1·0725	68	1·0674	94
1·0242	17	1·0552	43	1·0729	69	1·0660	95
1·0256	18	1·0562	44	1·0733	70	1·0644	96
1·0270	19	1·0571	45	1·0737	71	1·0625	97
1·0284	20	1·0580	46	1·0740	72	1·0604	98
1·0298	21	1·0589	47	1·0742	73	1·0580	99
1·0311	22	1·0597	48	1·0744	74	1·0553	100
1·0324	23	1·0607	49	1·0746	75		
1·0337	24	1·0615	50	1·0747	76		
1·0350	25	1·0623	51	1·0748	77		

Note.—The specific gravities above 1·0553 correspond to two solutions of quite different strengths. To determine whether a given acetic acid is above 78 per cent. (the maximum density), simply add a little water. If the specific gravity rises, then the acid was above 78 per cent., and *vice versa*.

10. SPECIFIC GRAVITY OF CAUSTIC SODA AT 6° F. (Lunge).

Degrees Baumé.	Degrees Twaddle.	Specific Gravity.	NaOH per Cent.	Degrees Baumé.	Degrees Twaddle.	Specific Gravity.	NaOH per Cent.
1	1·4	1·007	0·61	26	44·0	1·220	19·58
2	2·8	1·014	1·20	27	46·2	1·231	20·59
3	4·4	1·022	2·00	28	48·2	1·241	21·42
4	5·8	1·029	2·71	29	50·4	1·252	22·64
5	7·4	1·036	3·35	30	52·6	1·263	23·67
6	9·0	1·045	4·00	31	54·8	1·274	24·81
7	10·4	1·052	4·64	32	57·0	1·285	25·80
8	12·0	1·060	5·29	33	59·4	1·297	26·83
9	13·4	1·067	5·87	34	61·6	1·308	27·80
10	15·0	1·075	6·55	35	64·0	1·320	28·83
11	16·6	1·083	7·31	36	66·4	1·332	29·93
12	18·2	1·091	8·00	37	69·0	1·345	31·22
13	20·0	1·100	8·68	38	71·4	1·357	32·47
14	21·6	1·108	9·42	39	74·0	1·370	33·69
15	23·2	1·116	10·06	40	76·6	1·383	34·96
16	25·0	1·125	10·97	41	79·4	1·397	36·25
17	26·8	1·134	11·84	42	82·0	1·410	37·47
18	28·4	1·142	12·64	43	84·8	1·424	38·80
19	30·4	1·152	13·55	44	87·6	1·438	39·99
20	32·4	1·162	14·37	45	90·6	1·453	41·41
21	34·2	1·171	15·13	46	93·6	1·468	42·83
22	36·0	1·180	15·91	47	96·6	1·483	44·38
23	38·0	1·190	16·77	48	99·6	1·498	46·15
24	40·0	1·200	17·67	49	102·8	1·514	47·60
25	42·0	1·210	18·58	50	106·0	1·530	49·02

11. TABLE OF PERCENTAGE OF AQUEOUS AMMONIA SOLUTION AT 15° (Lunge and Wiernick).

The numbers given in the third column are corrections to be applied for the interval of temperature 13° to 17°. If, for example, the specific gravity has been found to be 0·900 at 13°, the value at 15° is found by subtracting $2 \times 0{\cdot}00057 = 0{\cdot}001$ from this number (0·900). One obtains the value 0·899, and therefore the percentage of ammonia is ¼ per cent. higher.

Specific Gravity.	Percentage NH_3.	Correction for ±1°.	Specific Gravity.	Percentage NH_3.	Correction for ±1°.
1·000	0·00	0·00018	0·940	15·63	0·00039
0·998	0·45	0·00018	0·938	16·22	0·00040
0·996	0·91	0·00019	0·936	16·82	0·00041
0·994	1·37	0·00019	0·934	17·42	0·00041
0·992	1·84	0·00020	0·932	18·03	0·00042
0·990	2·31	0·00020	0·930	18·64	0·00042
0·988	2·80	0·00021	0·928	19·25	0·00043
0·986	3·30	0·00022	0·926	19·87	0·00044
0·984	3·80	0·00022	0·924	20·49	0·00045
0·982	4·30	0·00022	0·922	21·12	0·00046
0·980	4·80	0·00023	0·920	21·75	0·00047
0·978	5·30	0·00023	0·918	22·39	0·00048
0·976	5·80	0·00024	0·916	23·03	0·00049
0·974	6·30	0·00024	0·914	23·68	0·00050
0·972	6·80	0·00025	0·912	24·33	0·00051
0·970	7·31	0·00025	0·910	24·99	0·00052
0·968	7·82	0·00026	0·908	25·65	0·00053
0·966	8·33	0·00026	0·906	26·31	0·00054
0·964	8·84	0·00027	0·904	26·98	0·00055
0·962	9·35	0·00028	0·902	27·65	0·00056
0·960	9·91	0·00029	0·900	28·33	0·00057
0·958	10·47	0·00030	0·898	29·01	0·00058
0·956	11·03	0·00031	0·896	29·69	0·00059
0·954	11·60	0·00032	0·894	30·37	0·00060
0·952	12·17	0·00033	0·892	31·05	0·00060
0·950	12·74	0·00034	0·890	31·75	0·00061
0·948	13·31	0·00035	0·888	32·50	0·00062
0·946	13·88	0·00036	0·886	33·25	0·00063
0·944	14·46	0·00037	0·884	34·10	0·00064
0·942	15·04	0·00038	0·882	34·95	0·00065

12. STRENGTH OF BLEACHING POWDER SOLUTIONS.
(Lunge.)

Specific Gravity.	Degrees Twaddle.	Available Chlorine.		Specific Gravity.	Degrees Twaddle.	Available Chlorine.	
		Grms. per Litre.	Grains per Gallon.			Grms. per Litre.	Grains. per Gallon.
1·1155	23·1	71·79	5025·3	1·0600	12	35·81	2506·7
1·1150	23	71·50	5005·0	1·0550	11	32·68	2287·6
1·1105	22·1	68·66	4806·2	1·0500	10	29·41	2058·7
1·1100	22	68·00	4760·0	1·0450	9	26·62	1863·4
1·1060	21·2	65·33	4573·1	1·0400	8	23·75	1662·5
1·1050	21	64·50	4515·0	1·0350	7	20·44	1430·8
1·1000	20	61·17	4281·9	1·0300	6	17·36	1215·2
1·0950	19	58·33	4083·1	1·0250	5	14·47	1012·9
1·0900	18	55·18	3862·6	1·0200	4	11·44	798·7
1·0850	17	52·27	3658·9	1·0150	3	8·48	593·6
1·0800	16	48·96	3427·2	1·0100	2	5·58	390·6
1·0750	15	45·70	3199·0	1·0050	1	2·71	189·7
1·0700	14	42·31	2961·7	1·0025	½	1·40	98·0
1·0650	13	38·71	2709·7				

13. SPECIFIC GRAVITY OF SOLUTIONS OF TANNIC ACID AT 15° (Trammer).

Specific Gravity.	Percentage Tannic Acid.	Specific Gravity.	Percentage Tannic Acid.	Specific Gravity.	Percentage Tannic Acid.
1·0040	1·0	1·0104	2·6	1·0172	4·3
1·0044	1·1	1·0108	2·7	1·0180	4·5
1·0048	1·2	1·0112	2·8	1·0184	4·6
1·0052	1·3	1·0116	2·9	1·0188	4·7
1·0056	1·4	1·0120	3·0	1·0192	4·8
1·0060	1·5	1·0124	3·1	1·0196	4·9
1·0064	1·6	1·0128	3·2	1·0200	5·0
1·0068	1·7	1·0132	3·3	1·0242	6
1·0072	1·8	1·0136	3·4	1·0324	8
1·0076	1·9	1·0140	3·5	1·0406	10
1·0080	2·0	1·0144	3·6	1·0489	12
1·0084	2·1	1·0148	3·7	1·0572	14
1·0088	2·2	1·0152	3·8	1·0656	16
1·0092	2·3	1·0160	4·0	1·0740	18
1·0096	2·4	1·0164	4·1	1·0824	20
1·0100	2·5	1·0168	4·2		

14. SPECIFIC GRAVITY OF SOLUTIONS OF TARTAR EMETIC AT 17·5° (Streit).

Specific Gravity.	Percentage Tartar Emetic.	Specific Gravity.	Percentage Tartar Emetic.	Specific Gravity.	Percentage Tartar Emetic.
1·005	0·5	1·015	2·5	1·031	4·5
1·007	1·0	1·018	3·0	1·035	5·0
1·009	1·5	1·022	3·5	1·038	5·5
1·012	2·0	1·027	4·0	1·044	6·0

15. SPECIFIC GRAVITY OF SOLUTIONS OF SODIUM BISULPHITE AT 15°.

Specific Gravity.	Percentage $NaHSO_3$.	Percentage SO_2.	Specific Gravity.	Percentage $NaHSO_3$.	Percentage SO_2.
1·008	1·6	0·4	1·171	16·5	10·2
1·022	2·1	1·3	1·190	18·5	11·5
1·038	3·6	2·2	1·210	20·9	12·9
1·052	5·1	3·1	1·230	23·5	14·5
1·068	6·5	3·9	1·252	25·9	15·9
1·084	8·0	4·8	1·275	28·9	17·8
1·100	9·5	5·7	1·298	31·7	19·6
1·116	11·2	6·8	1·321	34·7	22·5
1·134	12·8	7·8	1·345	38	23·6
1·152	14·6	9·0			

16. SPECIFIC GRAVITY OF SOLUTIONS OF SODIUM ACETATE AT 17·5° (Gerlach).

Specific Gravity.	Percentage CH_3COONa.	Percentage $CH_3COONa+3H_2O$
1·015	3·015	5
1·031	6·030	10
1·047	9·045	15
1·063	12·060	20
1·0795	15·075	25
1·096	18·090	30
1·113	21·105	35
1·1305	24·120	40
1·1485	27·135	45
1·1670	30·150	50

17. WEIGHTS AND MEASURES.

METRIC SYSTEM.

1 gramme (grm.) = 15·43 grains (grs.).
1 kilogramme (kilo.) = 1000 grms. = 15,430 grs. = $2\frac{1}{8}$ lbs. nearly.
1 cubic centimetre (c.c.) = 17 minims = $\frac{1}{284}$th gill.
1 litre = 1000 c.cs. = 35 ozs. nearly = $3\frac{1}{2}$ gills nearly.
1 metre = 100 centimetres (cms.) = 1·093 yards.

ENGLISH SYSTEM.

1 ounce (oz.) = 28·35 grms.
1 pound (lb.) = 16 ozs. = 453·6 grms. = 0·4536 kilo.
1 gill = 2 noggins = 10 ozs. = 0·284 litre.
1 pint = 4 ,, = 20 ozs. = 0·567 ,,
1 quart = 8 ,, = 40 ozs. = 1·135 ,,
1 gallon = 4 quarts = 8 pints = 16 gills = 32 noggins = 10 lbs. = 4·543 litres.
1 inch (″) = 2·54 centimetres (cms.).
1 foot (′) = 12″ = 30·48 cms.
1 yard = 3′ = 91·4 cms. = 0·914 metre.

ADDENDA.

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Solvitex B.G. and Solvitex S.T.—These two new thickening agents, recently introduced by W. A. Scholten's Chemische Fabrieken, Groningen, Holland, consist of modified starches, in fine granular form, which possess the valuable property of dissolving perfectly when sprinkled or poured steadily into vigorously stirred *cold water*, the stirring being continued for half an hour or longer until every particle of the material is dissolved. No boiling is necessary except in cases where Solvitex is used in admixture with starch. On no account must water be added to, or poured over, the dry powdered thickening agents, otherwise they form a sticky mass which cannot afterwards be got into solution.

Although Solvitex thickenings are made from starch, their solutions possess properties wholly different from those of thickenings obtained by boiling ordinary starches and British gums with water. They are manufactured by processes which bring about both chemical and physical changes in the starch aggregate, whereby the printing quality of the thickening is greatly improved in comparison with that of starch paste, especially in respect of sharpness of impression and evenness of shade. They give smooth, soft thickenings of gum-like consistency and of such stability that they may be kept for long periods without undergoing decomposition or breaking up into a curdy mass of thickening and water.

Both brands of Solvitex may be mixed (as solutions) with starch in any proportion. Neither brand is precipitated by chromium salts or tannic acid, nor is either affected by alkali, so that both are suitable for practically any style of work. The S.T. brand used with starch is well adapted to the printing of Azoic colours of all types, Aniline black and steam colours (Basic and Chrome colours, etc.), whilst a thickening composed of the B.G. brand and wheat starch is specially recommended for printing strong Vat colours and blacks in cases where sharp impressions of finely engraved patterns are required in dark shades, *e.g.* shirting prints.

Solvitex thickenings have a slightly alkaline reaction and must be neutralised or acidulated when employed with Chrome and Basic dyestuffs, Aniline black, the Indigosols and Soledons (steaming process) and other colouring matters or mordants which are applied in an acid medium. Solvitex B.G. and Solvitex S.T. may replace British gum and gum tragacanth respectively for all purposes for which these two gums are used in admixture with starch.

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Nafka Crystal Gum.—Under this name the makers of Solvitex thickening agents have introduced a highly refined natural gum product which serves as an excellent substitute for gums of the Senegal and Arabic types. It possesses three or four times the thickening power of unrefined natural gums, is readily soluble in hot or cold water, and, being entirely free from sand, grit, chips of bark, woody fibre, and colloidal matter, it is prepared quickly for printing. From a practical standpoint this absence of foreign matter is a great advantage since, in addition to doing away with the necessity for allowing the solution to stand in order to let impurities settle, it reduces to a minimum the risks of faulty printing due to streaks, scratches, "sticking-in," etc., in so far as these faults arise from defective thickening.

Nafka Crystal Gum yields smooth, even shades in blotches and gives

sharp impressions of small objects and fine lines. It is suitable for printing Basic, Vat, and Sulphur dyestuffs and various discharge styles, but it cannot be used for Azoic colours of any description nor for Chrome colours. It may be employed either alone or in combination with starch, Solvitex, British gum, or gum tragacanth, according to the class of work in hand. Used alone, it gives very even prints with pale shades of Vat colours in large objects or blotches. It is also used alone for hand block printing, screen printing, and spray printing. Owing to its excellent solubility, Nafka Crystal Gum is well adapted to the printing of delicate silk and rayon fabrics, from which it is removed easily during the final washing processes after printing.

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Ciba Naphthol R.P.—Amongst the many naphthols which have been brought out with a view to improving the quality of Azoic colours produced on the fibre, Ciba Naphthol R.P. is unique in that it is the only coupling component of any interest whatsoever to calico printers that is derived from α-naphthol. In chemical structure it also differs from the better known β-naphthol derivatives in general use. The true naphthol derivatives of the great Naphthol A.S. and Brenthol groups are all arylamides of β-hydroxy-naphthoic acid, whereas Ciba Naphthol R.P. is a benzoyl substitution product of α-naphthol, its constitution being 1-hydroxy-4-benzoyl naphthalene or better, perhaps, 4-benzoyl-α-naphthol. The commercial product is a mixture of the pure substance and sodium sulphate.

Ciba Naphthol R.P. is characterised by an extraordinary resistance to steam ; even after $\frac{3}{4}$–1 hour's steaming, under pressure, in a cottage steamer, it retains undiminished its capacity for coupling completely with diazo compounds, and yields shades of unimpaired fullness and brightness. In this respect it stands alone for the production of certain styles which depend upon the printing of *long-steam* Mordant colours on naphthol prepares, the printed and steamed goods being subsequently developed through diazo solutions in a padding machine. Such styles, however, are executed usually by equally good and more expeditious methods employing Naphthol A.S. or Brenthol A.S. ; consequently the resistance to prolonged steaming is of less importance to-day than was the case formerly. Nevertheless, it is a valuable property and, as most naphthols are affected to a greater or less extent by even a *short* steaming, a property well worth consideration in the execution of resist styles in which steaming precedes development in diazo solutions.

Another small advantage possessed by Ciba Naphthol R.P. is that, having no affinity for the cotton fibre, the uncoupled naphthol is very easily washed out from the unprinted parts of direct prints.

In other respects Ciba Naphthol R.P. has no outstanding points of interest for printing purposes. It yields a limited range of fast bright colours of about the order of those given by some of the better known naphthols, but it is not a serious competitor of these latter, and it is difficult to see what reasons, apart perhaps from those commercial, dictated its introduction.

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